

# **Development of Polymeric Auxiliaries for Salt Free Neutral Reactive Dyeing of Cotton Textiles**

**A Major Project submitted to Faculty of Technology  
of  
University of Delhi**

**Towards the Partial fulfillment of the requirements for award the Degree**

**Master of Engineering  
In  
Polymer Technology**

**Submitted by:**

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**Under the Kind Guidance of**

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## CERTIFICATE

This is to certify that the Major Project entitled “**Development of Polymeric Auxiliaries for salt free Neutral Reactive dyeing of Cotton Textiles**” is being submitted by **Mr. Manoj Kumar** in partial fulfillment of the requirement for the award of **Master of Engineering** degree in **Polymer Technology** to **Delhi College of Engineering, University of Delhi, Delhi**, is a record of bona-fide work carried out by him under our guidance and supervision.

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**Place: Delhi**

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## **Introduction**

Reactive dyes are widely used to dye cellulosic because of their good wash fastness properties. However, the process of dyeing with reactive dyes is a pollution generating process & also energy & water intensive. One of the most serious ecological problems that arrive from the reactive dyes is the high salt content in the effluent. High sodium chloride or sodium sulphate concentration in the range of 30-100 g/l are required to increase their substantivity towards cellulose by decreasing the negative charged barriers between the cellulose & dye anions & also by reducing the solubility of the dyes. Sodium sulphate increases the accumulations of the sulphate ions, which is associated with the increase in acidity of the water bodies.

It is becoming the great problem these days, because the effluent from textile industries is directly release to the soil or rivers. In western India, where lots of industries are involved in dyeing cotton, this problem is in their worst condition. The effluent is completely destroying the fertility of the soil. Ground water of the effected areas is also not drinkable.

So, to avoid such types of problems here we adopt some novel concepts for salt free reactive dyeing of cotton. One such interesting idea is based on pretreatment of cellulosic fibre using a High molecular weight Polymeric auxiliary & also a Lower molecular weight cationic agent.

Details of the topic and the experimental method applied for this novel concept are in the subsequent pages.

# Cotton

Cotton has supplied man with fiber, a basic necessity of life, since prehistoric times. The oldest archeological record of the use of cotton as a textile, dating back to about 3000 BC, was found in the valley of the Indus River. Apparently, the cotton first use by humans came from perennial varieties that grew as trees, chiefly in tropical & subtropical regions. The commercial cultivation of the cotton in India was mentioned in ancient Hindu laws and religious books as early as 1500 BC. Greek writers reported during the period 500-300 BC that India had wild trees bearing fleeces. During the thirteenth century, Marco Polo recorded the production and manufacture of cotton in Asia. With the development of annual varieties in India, china, Asia Minor, and Arabia, cotton become more available as a textile fiber. During the ninth and tenth centuries, cotton varieties were introduced into Sicily and Spain. In the sixteenth century Spanish explorers found cotton being cultivated and manufactured into fabrics from the West Indies to Peru. Early explorers also found wild cottons growing in the area of Texas and Louisiana.

## Fibers

**Chemical Structure.** In 1838 Payen reported that a common fibrous substance, which was later termed Cellulose, was found in all plant materials. At that time the term lignin was a collective term and was recognized as a complex mixtures of the substances. Cotton fibers were purified by acid and ammonia treatment, followed by extraction with water, alcohol and ether. This method is remarkably similar to purification methods used a century later.

The calculated composition of cellulose was based on the conclusion that cotton cellulose is a high polymer consisting of units of anhydroglucose with the empirical formula,  $(C_6H_{10}O_5)_n$  and structure.

The degree of polymerization, for cellulose can be as high as 4000-5000, giving molecular weights up to 800000. Because of the polydispense nature of the cotton cellulose, molecular weights determined by different methods may be yield different values.

Cotton cellulose is polymorphic in nature, that is, it crystallizes in different forms. Crystalline lattice type I is the most common natural structure. It may be irreversibly changed to lattice type II by a swelling reagent, such as aqueous sodium hydroxide, in a process termed mercerization.

## **Composition**

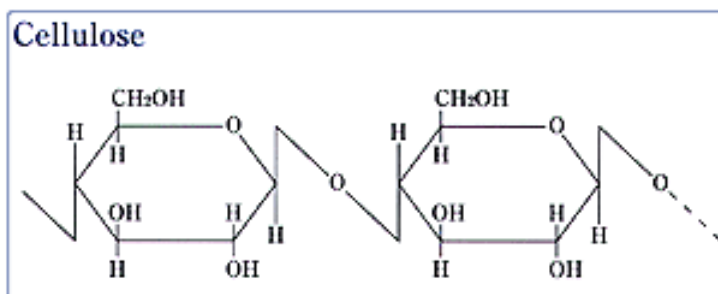
The compositions of a typical mature cotton fiber, as harvested and after purification, including regain moisture are shown in the table. The protein occurs chiefly in the fiber lumen with a small amount in the primary wall. It is probably a protoplasmic residue left upon the death of the growing cell. Wax, pectic acid, and related compounds are found in the primary wall. The wax influences wetting properties, provides lubrication, and tends to decrease cohesion between the fibers and consequently the tensile strength of the yarns. Some non-commercial cotton varieties contain more than 15% wax. Water content is influenced by the temperature and the relative humidity under which it is measured. Constituents of the inorganic ash are, in decreasing amounts, potassium, magnesium, calcium, sodium, sulfur, chlorine, phosphorous, aluminum, silicon, and iron. The fiber, as harvested, may be purified by extraction with wax solvents followed by boiling with dilute solutions of sodium hydroxide, neutralizing with a weak acid, and washing with water.

## **Chemical Modification**

Heterogeneous alkylation and acylation are the two most common ways to modify the properties of cotton without changing its physical form, particularly at low degrees of substitution. The properties of fibrous cellulosic esters or ethers are dependent on the

Typical compositions of Cotton Fiber		
Constituent	Lint, %	
	Harvested	Purified
Cellulose	88.8	92-94
Protein	0.9	
Inorganic Ash	0.5	<0.1
Wax	0.7	
Pectic Acid	0.9	
Other organic acids	0.5	
Sugars	0.1	
Other constituents	0.8	
Water	7	6-8

Chemical reagent used; degree and uniformity of substitution, degree of polymerization of the cellulose comprising the cotton; and catalysts, plastisizers or experimental condition used.



**Structure of Cellulose**



Heterogeneous alkylation and acylation are the two most common ways to modify the properties of cotton without changing its physical form, particularly at low degrees of substitution. The properties of fibrous cellulosic esters or ethers are dependent on the chemical reagent used; degree and uniformity of substitution, degree of polymerization of the cellulose comprising the cotton; and catalysts, plasticizers or experimental condition used.

Cellulose, a polyhydroxy compound, may be modified by typical alcohol reactions, but the natural physical properties and morphological structures of cotton fibers place limitations on the chemical reactivity of cellulose. For example, cotton cellulose has accessible and inaccessible regions. Amorphous regions of low molecular order are accessible; crystalline regions of high molecular order are inaccessible.

Many attempts have been made to relate the properties of chemically modified cotton to the degree of substitution, i.e., the average number of reacted hydroxyl groups per anhydroglucose unit, ranging from 0 to 3. Conditions must be carefully controlled to yield chemically modified cottons with reproducible properties.

Cotton reacts topochemically, first on the surface and in the accessible regions of the fiber. In most cases the reagents are dissolved or dispersed in a liquid medium that wets the cotton fibers. One procedure is to allow the reaction of the fibers may be either under tension or slakes and may be stretched after the reaction is completed. In another method, solution is padded on the cotton fiber to the desired amount. The solvent is evaporated, and the reaction with the cotton fiber is initiated by heating. Solid-gas phase reactions, such as occur in weathering degradation, are also observed.

## **GENERAL PROPERTIES OF DYESTUFFS**

A chromogen having auxochromes deepening of the colour takes place. The auxochromes also impart another property, that of affinity for textile fibers. Thus when an amino group is present in a direct dye, the dyestuff molecule can be held in cellulosic fiber by the formation of hydrogen bonds between the hydroxy groups of cellulose and the amino groups of the direct dye.

The hydroxy groups of cellulose play an important part in forming a dye-fiber bond, i.e. imparting affinity to the dye for cellulose. This is evident from the observation that when cellulose is acetylated (hydroxy groups are converted into acetate groups) as in the case of cellulose acetate or triacetate rayon, the affinity of the direct dye for the modified fiber vanishes: the affinity is again restored when these acetate groups are reconverted into hydroxy groups by hydrolysis

### **Linearity**

The affinity of the dye is connected with the linearity of the molecular structure of the dye, so that they can lie with their long axis parallel to the axis of cellulose molecule, which is also linear. Direct dyes have a linear structure as shown below: -

### **Coplanarity**

For a direct dye to have affinity for cellulosic fibers it is not enough to have a linear molecule, the aromatic rings present in the dye molecule must be coplanar (they should lie in the same plane). This is seen in the following pair of dyes.

The steric hindrance offered by the two-methoxy groups, is to be in the same plane and they become non-coplanar. As a result, the dye loses its affinity for the cellulose In Benzo-purpurine 4B, the methoxy groups are ortho to the azo and two

benzene rings are coplanar (there is no steric hindrance in this dye). Hence it has affinity for cellulose.

## Fastness Properties

When a dye is present on a fabric it is expected to have certain fastness properties. For example when a dyed or a printed cloth (curtain material, garments etc.) is exposed to sunlight during its use the dye should not change its colour or fade. i.e.. it should have good light fastness. During the exposure of the dyed fabric to sunlight the complementary colour is absorbed by the dye. Blue and green dyes absorb orange and red portions of the VIBGYOR region (visible light) respectively and yellow and orange dyes absorb in the violet and blue portions respectively - Violet and blue light rays have shorter wavelengths (and hence higher energy) than orange and red light rays. The energy absorbed by the dye may bring about the self-destruction of the dye in the presence of oxygen and moisture (i.e. air); alternatively, the absorbed energy may be transferred by the dye to the cloth, which is then damaged in the presence of air. Good dyes should be free from both these defects.

Light fastness of a dye on a particular fiber is expressed in terms of Grades 1 – 8:

Grade 1	Very good
Grade 2	Poor
Grade 3	Fair
Grade 4	Very good
Grade 5	Good
Grade 6	Very good
Grade 7	Excellent
Grade 8	Outstanding

The dye must possess good washing fastness if the cloth on which it is dyed or printed is to be used for making garments otherwise staining of the garments with dyes stripped from other garments occurs during washing of many garments together. These dyes should also possess good perspiration fastness. Perspiration of some people is acidic in nature, and of others, alkaline. When the dye does not have good perspiration fastness, and when people wearing clothes dyed with the dye, perspire, a part of the dye coming in contact with the perspiration is stripped from the cloth and stains the undergarments or the skin of the wearer.

The dyes intended for colouring dress materials should have good rubbing fastness also. For example the cuffs and collars of shirts are constantly rubbed against the wrists and the neck of the wearer. If the dyeing process is not done properly some of the dye particles may be mechanically held loosely on the fabric surface and these particles rub out easily on the wearer's skin coming into contact with the cloth.

Some of the dyes especially disperse dyes dyed on polyester, nylon, cellulose acetate, rayon etc., are susceptible to chemical damage by certain gases like nitrogen dioxide and sulphur dioxide present in the air in places where large amounts of coal are burnt or where dyestuff factories are located. This type of dye degradation is known as gas fading. Disperse dyes should have good fastness to gas fading. —Dyed polyester and nylon fabrics are subjected to high temperatures (180°C to 210°C during their processing in textile mills and are ironed during their use by the consumer. At high temperatures some of the disperse dyes sublime off. Therefore, disperse dyes should have good sublimation fastness.

Some of the cotton fabrics (dhotis and saris with coloured borders and fabrics with coloured checks or stripes) contain white and coloured yarns and a white and coloured design is produced during weaving itself. When such cloth is bleached, the dye used for producing the coloured yarns should withstand the bleaching action. Bleaching powder or sodium hypochlorite is generally used for bleaching. Hence these dyes should have good chlorine fastness.

A dye need not have very good fastness to all the above agencies (light, washing, perspiration, rubbing, gas fading, sublimation, chlorine etc). For example, a dye used for colouring the curtain cloth need not be fast to perspiration but must have very good light fastness. Dyes for garment materials should be fast to washing, light, perspiration and rubbing. Dyes intended for polyester fabrics should have very good sublimation fastness and very good fastness to gas fading. Therefore, dyes have to be chosen depending on the use to which the dyed or printed fabric is put to.

Different classes of dyes possess these fastness properties to different extents. Even dyes belonging to the same class can have widely varying fastness properties.

The various fastness properties of dyes on fibers (except light fastness) are given Grades 1-5 (Grade 1 is very poor and Grade 5 is excellent). In order to find out the fastness grades certain tests are made. For this purpose, the dyed cloth piece (10 cm x 4 cm) is sandwiched between two undyed cloth pieces (5 cm x 4 cm) and stitched along the edges leaving 5 cm x 4 cm of the dyed piece exposed. This composite piece is placed in a soap solution (5 g/l) and treated at 40°C for 30 minutes (washing test No. 1), at 50°C for 45 min (washing test No. 2) treated with soap solution (5 g/l) containing sodium carbonate (2 g/l) at 60°C for 30 min (washing test No. 3), and at 95°C for 30 min (washing test No. 4). In these cases washing treatment of increasing severity is given and in each test washing fastness grades are given after observing the cloth pieces and noting the loss of colour from the dyed piece and staining of the adjacent undyed piece. The grading is done as follows —

<b>Dyed piece</b>		<b>Undyed piece</b>	
Observation	Grade	Observation	Grade
Considerably changed	1	Considerable staining	1
Slightly changed	3	Slightly stained	3
Virtually unchanged	5	Virtually unstained	5

For assessing perspiration fastness, the composite piece, prepared as above is treated with artificial perspiration solutions

1-Histidine hydrochloride monohydrate	0.5	g
Sodium chloride	5.0	g
Disodium hydrogen phosphate	2.5	g
Distilled water	1000	ml

The pH of the above solution is adjusted to 8 (alkaline perspiration and to 5.5 (acidic perspiration).

The composite piece is placed in the artificial perspiration solutions (separately) at the room temperature for 30 mm. taken out, placed between two glass plates and pressed by placing a weight of 4.5 kg. and allowed to stand in an oven at 37<sup>0</sup>C for 4 hours. The pieces are separated and the charges in the depth of colour of the dyed piece and staining of the adjacent undyed pieces noted and the fastness grades are given as in washing fastness testing (Grades 1, 3 and 5).

The chemical structure of a dye has a tremendous influence on the fastness properties of dyes as well as on the colour of the dyes. Thus in a series of disperse dyes of the type colours ranging from yellow to blue can be obtained.

When dyed fibers are exposed to light, the dye may change in colour (this effect is called phototropism) or may undergo permanent fading. These changes may be represented as follows

Even though phototropism is a defect, it may be advantageously used in increasing the light fastness of the dye it is possible to alter the phototropic behavior of the dyes by introducing certain constituents in suitable positions in the dyestuff molecule. For

example the introduction of an electron-withdrawing group like a nitro group in a position para to the azo makes the dye non-phototropic as in the following pair of dyes

In the azo disperse dyes the presence of a minimum number of attackable groups in the dyestuff molecule increases the light fastness of the dye. An increase in the electron mobility of the dye molecule decreases the light fastness as shown by the progressively decreased light fastness of the following series of compounds: -

The substitutions produce bath chromic shifts and this is achieved only at the cost of light fastness and, therefore, a compromise has to be struck. This behavior has been found in anthraquinone dyes also. For example, the exposure time required for fading is, 160,60 and 20 hours for the dyes A, B and C respectively.

## Dyeing with Reactive dyes

The introduction of reactive dyes (Procion Yellow R, Brilliant Red 2B, and Blue 3G) by ICI in 1956 is an important landmark in the history of synthetic dyes. Earlier, the application of dyestuffs to textile materials involved: -

1. Physical adsorption of water soluble dyestuffs from an aqueous medium by the fibre by reversible attachment to active sites present in the fibre (direct dyes on cellulose held by hydrogen bonds and acid dyes held in protein fibres by salt links)
2. Mechanical retention of water-insoluble dyes in the fibre substance, the application involving temporary solubilization before applying to be eventually reconverted into the insoluble form (vat and sulphur dyes on cellulosic fibres)
3. Dissolution of the dyestuff in the fibre substance (disperse dyes in polyester fibres).

A fourth principle of dyeing was applied to dyeing and printing with the appearance of reactive dyes. These dyes chemically reacted with the fibres (hence the name reactive dyes) with the formation of a covalent bond between the dye and the fibre as shown below: -

Simultaneously with the reaction of the dye with cellulose, a certain amount of the dye reacts with water, thereby removing the particular reactive group from the dye; when this happens, the dye is said to be hydrolyzed as shown below: -

Both of the above reactions take place in the presence of an alkali like soda ash or caustic soda.

The reactivity of these dyes is due to the chlorine atoms attached to the triazine ring. When two chlorine atoms are present in the dye molecule, as in the case of Procion Yellow R, one of the chlorine atoms is so reactive, that it reacts with cellulose even at room temperature (20<sup>0</sup> to 30<sup>0</sup>C) in the presence of an alkali. Hence such reactive dyes



(dichlorotriazine dyes) are called cold brand reactive dyes. When only one chlorine atom is present in the dyestuff molecule, the reactivity of the dye decreases considerably and the dyeing has to be carried out at a higher temperature (65<sup>0</sup> to 80<sup>0</sup>C). Hence these dyes are called hot brand reactive dyes.

When an alkaline solution of a dichlorotriazine (cold brand) reactive dye is kept for some time various products are formed. Thus when Procion Yellow R is kept in contact with soda ash solution (25 g/l) at 60<sup>0</sup>C, the appearance of monochloro-monohydroxy and of dihydroxy dye and the disappearance of the dichloro dye are shown in Fig.

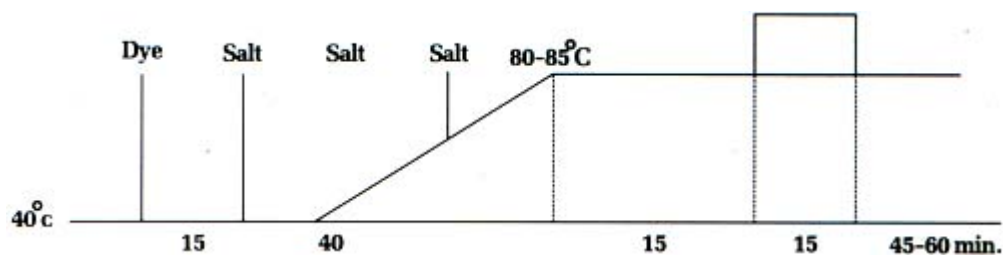
It is seen that the concentration of the dichloro dye drops continuously and after 75 mm. it's about 10% of the original concentration. Since this dye reacts with water in two stages the concentration of the monochloro-monohydroxy dye initially increases and then decreases while that of the dihydroxy compound increases continuously. The dihydroxy compound can react with the fibre, while the monochloro-monohydroxy dye (this becomes hot brand dye) does not react with the fibre under the conditions of dyeing cold brand dye. As a consequence of this water at temperatures higher than 40<sup>0</sup>C should not be used and the solution not be kept for any length of time before use.

## **Reactive dyes**

Reactive dyes are known for their bright colours & very high to excellent light fastness & wash fastness, through poor resistance to chlorine bleach. There are several broad classes of reactive dyes. Most are intended for cellulose fibres, but some are specially intended for wool. The most popular reactive dye family for textile artists is the **Procion H-E, Remazol, and Cibacron**.

Reactive dyes may be more expensive than other dye families suitable for the same fibres, especially when very dark or dull colours are considered. They are the newest class of the textile dyes first introduced commercially, for cellulosic fibers in 1956, one hundred years after the development of the first synthetic dye. Within the family the range of colour available as “pure” dyes is typically quite small. Against this, reactive dyes of the same family can generally be mixed to produce a very wide range of colours, while retaining the good application characteristics and brightness. The reactivity among families varies widely, so some are easily applied at room temperature, some at boiling temperature and others at intermediate temperature. All types are suitable for exhaust dyeing and many type are suitable for pad-batch dyeing & for printing. Apart from cost, the biggest commercial drawbacks to reactive dyes are that they require large amount of electrolyte in most processes, and extensive rinsing and hot washing after dyeing to remove unfixed and hydrolyzed dye.

## PROCION HOT BRAND REACTIVE DYES



**Standard Exhaust Method for Hot Brand Reactive Dyes**

Depth of Shade %	Salt g/l (Dye Liquor)	Soda Ash g/l (Dye Liquor)
Up to 0.5	40	20
0.5 to 2.0	60	20
2.0 to 4.0	80	20
Above 4.0	100	20

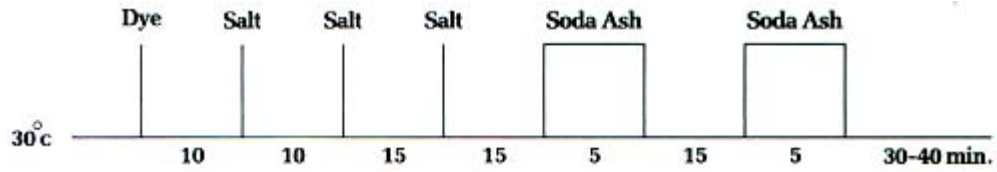
### Depth of shade for Hot Brand Reactive Dyes

#### Hot Brand Dyes Shade Card

Reactive Hot brand Dyes		FASTNESS PROPERTIES				
		Light	Washing	Perspiration	Hypochlorite	Dischargeability
Yellow H7GL Yellow - 57		6	5	5	2	G
Yellow H4G Yellow - 18		6	5	5	1	G
Gol. Yellow		6	5	5	3	F

HR Yellow – 12						
Orange H2R Orange – 13		4	5	4	4	P
Red H8B Red – 31		4	4	4	3	P
Red 6BX Red – 76		4	4	5	2	P
Red Brown H4R Brown – 9		4	5	4	5	P
Magenta HB Violet – 13		4	4	4	1	F
Purple H3R Violate – 1		6	4	5	4	P
Black HN Black – 8		5	4	5	4	P
Blue H5R Blue – 13		5	5	5	1	P
Blue H2R		4	4	4	2	P
Blue H3RP Blue – 49		4	5	4	2	P
Tur. Blue H5G Blue – 25		5-6	4-5	3	3-4	P
Navy Blue RX Blue – 59		3	3-4	4-5	1	P

## PROCION COLD BRAND REACTIVE DYES



### Standard Exhaust Methods for Cold Brand Reactive Dyes

Depth of Shade %	Salt g/l (Dye Liquor)	Soda Ash g/l (Dye Liquor)
Up to 0.5	30	3
0.5 to 2.0	40	4
2.0 to 4.0	50	7
Above 4.0	60	10

### Salt & Alkali Requirement for Cold Brand Reactive Dyes

## Shade Card for Procion Cold Brand Dyes

Reactive Cold Brand Dyes		FASTNESS PROPERTIES				
		Light	Washing	Perspiration	Hypochlorite	Dischargeability
Red M5B Red - 2		4-5	4-5	3-4	1	P
Red M8B Red - 11		4-5	4-5	2	4	P
Magenta MB Voilet - 13		4-5	5	4-5	1	F
Orange M2R Orange - 4		5	5	4	4	P
Orange M2RJ		3-4	4	4	4-5	P
Gol. Yellow MR Yellow - 44		5	4-5	4	1	P
Yellow MR EX H/C Yellow - 44		5	4-5	4	1	P
Yellow M3R Yellow - 36		6	5	4	2	G

Yellow M4R Orange - 14		5	4-5	4	1	P
Yellow M8G Yellow - 86		6	4-5	4-5	1	G
Yellow M4G Yellow - 22		6	4	5	1	G
Yellow MGR Yellow - 7		6	5	4-5	4-5	P
Violet C4R Violet - 12		4	3	4	1	P
Violet C2R Violet - 14		3-4	3	4	1	P
Blue MR Blue - 4		6	5	5	2	P

## **Reactivity and affinity of the Reactive Dyes**

If the reactivity of the dye is increased considerably, the rate of reaction with the fibre increases. Therefore, the dyeing can be carried out in a short time. However, in this case the rate of hydrolysis of the dye also increases, leading to deactivation of a part of the dye. This results in wastage of the dye. If, on the other hand, the reactivity of the dye is decreased, the extent of hydrolysis can be reduced considerably. However this results in the slower rate of reaction with the fibre also the ultimate object of dyeing is to react as much of the dye as possible with the fibre and minimize the hydrolysis of the dye

This is achieved in practice in two stages. The dyeing is first started from the aqueous medium under neutral conditions when the dye does not react either with the fibre or with water. Then Glauber's salt or common salt is added to exhaust the dye onto the fibre as much as possible. In this respect, this stage of dyeing (exhaustion) resembles the dyeing of direct dyes on cotton. Then the second step (that of fixation or reaction with the fibre) is carried out by adding the alkali (usually soda ash). Since the exhausted dye is already on the fibre, it is more likely that the exhausted dye reacts with the fibre in preference to water. However, the dye present in the dyebath (which contains a substantial amount of the inactive dye) can now react with water since it is under alkaline conditions. It is already stated that the hydrolyzed dye cannot further react with the fibre but due to the affinity forces, it is adsorbed by the fibre and is retained in it. During the subsequent washing or soaping the substantively held hydrolyzed dye gets stripped into the washing bath thereby reducing the washing fastness of the dyeing. If the affinity of the original dye is reduced to a very low value this problem will not arise, and a rigorous treatment of the dyeing with boiling soap or detergent solution removes almost all hydrolyzed dye. However, if the affinity is very low, exhaustion of the dye bath prior to fixation cannot be achieved substantially. This result is a larger amount of the reactive dye remaining in the dyebath and getting hydrolyzed when alkali is added subsequently. If the dye has high affinity for cellulose like a direct dye, it becomes difficult to remove the hydrolyzed dye from the dyeing since it is also adsorbed by and retained in the fibre by fairly strong affinity forces, though not as strong as the covalent bond formed between



the dye and the fibre. Hence in actual practice low affinity dyes are selected or converting into reactive dyes.

Dyeing of reactive dyes, as in the case of many other classes of dyes, can be carried out by batch dyeing processes and by Continuous dyeing processes.

For batch wise dyeing of cellulosic fibre materials with cold brand reactive dyes, the following factors are important (Procion Dyestuffs in Textile Dyeing, ICI 1962)

- (1) The pH of the dyebath
- (2) The temperature of dyeing,
- (3) The concentration of the electrolyte,
- (4) The time of dyeing
- (5) The liquor ratio.

### **The pH of the dyebath**

The optimum pH of the dyebath for fixing cold brand reactive dyes on cotton and viscose rayon depends on the individual dyes, the temperature and time of dyeing, the pH decreasing with increasing temperature and time of dyeing. For most of the dyes the optimum pH is 10.8 to 11.0 at 20°C to 25°C. Soda ash has been the best alkali for dyeing at 30°C for cotton, mercerized cotton and linen. Increased fixation (due to high temperature) and increased dyebath stability and better reproducibility are the advantages of soda ash as the fixing agent. For viscose rayon, the optimum pH is 10.3 at 20<sup>o</sup> to 25<sup>o</sup> C.

## Amount of alkali

The amount of alkali used for fixing depends on the depth of shade dyed and the liquor ratio employed. Some quantities of alkali required for fixing the reactive dyes are given in Table

### Quantities Of Alkali (G/L) For Fixing Cold Brand Reactive Dyes By Batchwise Method For Cellulosic Fibres

Shade %	Soda ash liquor ratio			Caustic soda flakes		
	5:1	10:1	20:1	30:1	40:1	50:1
Upto 0.5	5	5	2	2	1	1
0.5-2.0	10	5	3	2	2	2
2.0-4.0	15	10	5	4	3	4
More than 4.0	20	15	10	5	5	6

## Dyeing Temperature

Since increase in temperatures affects the rate of physical and chemical processes involved in dyeing, it is important if dyeing reactive dyes also. The affinity of the dye for the fibre decreases with increases in temperature (the dyeing being an exothermic process), and at the same time the rate of hydrolysis of the dye increases and adversely affects the fixation of colour yield. However, the rate of diffusion of the dye in the fibre increases with increased temperature. At temperatures lower than 20°C, the rate of

fixation is very low. Hence for most of the dyes a temperature of 20°C to 25°C is the recommended temperature, while for some others dyeing at 50° to 60°C with sodium bicarbonate as the alkali gives maximum colour value.

### **Electrolyte Concentration**

Since reactive dyes have low affinity for cellulose, the fixation can be increased by exhausting the dyebath by adding common salt or Glauber's salt prior to fixation. The amount of the salts required to produce adequate exhaustion decreases with decreasing liquor ratio. Thus for pale shades on cotton and viscose rayon 15 and 10 g/l of common salt or anhydrous sodium sulphate respectively may be used. The quantities may be increased to 30 and 20 to 30 g/l for medium and deep shades on these fibres.

### **Time of dyeing**

Generally the dye may be added in two portions. The salt may also be added in two lots. The exhaustion takes place in 20 to 30 minutes. There is generally no advantage in extending the period beyond 30 min. The alkali is then added (also in two lots) and the dyeing continued for 30 to 90 minutes. The depth of shade and the reactivity of the dye decide the time of dyeing. For deeper shades, longer times are required.

### **Liquor ratio**

With decreased liquor ratio, both exhaustion and fixation take place to increased extent. However, the rate of fixation of most of the dyes is not significantly affected. As the Liquor ratio is decreased, the effectiveness of increasing salt addition also decreases. Hence lower amounts of salt are sufficient, to get optimum exhaustion.

## Dyeing of hot brand reactive dyes

In this case the dye is not as reactive as the cold brand dyes and hence higher temperatures have to be employed for achieving adequate fixation. The pH of the dyebath depend on the temperature of dyeing, which is in the range of 65°C-80°C for cotton and viscose rayon. Trisodium phosphate or mixture of soda ash and caustic soda is the recommended alkali. The quantities of alkali are given in Table.

### Amounts of Alkali For Hot Brand Reactive Dyes

Alkali	For cotton & linen	For viscous rayon
Trisodium phosphate	15 g/l	-----
Soda ash+ Caustic soda	20 g/l 1.5 g/l	----- -----
Soda ash	-----	10-20g/l

As with cold brand reactive dyes, an increase in temperature generally results in weaker shades of hot brand reactive dyes because of the decreased affinity at higher temperature and the consequent reduced fixation. Similarly lower temperatures reduce the reactivity and hence produce lower colour value unless the dyeing time is prolonged or the pH increased. Larger amounts of common salt or anhydrous sodium sulphate should be used for exhaustion (50 g/l, 75 g/l for shades of up to 1% 1 to 3% and above 3% respectively). The dyeing time is generally the same as in the case of cold brand reactive dyes.

## Vinyl sulphone reactive dyes

Reactive dyes belonging to another reactive system (vinyl sulphone system) have also become popular with the dyers as those belonging to the chlorotriazine system. Remazol dyes of F Hoechst AG and Navictive dyes of IDI Ltd., belong to this group of reactive dyes. These are marked in the form of sulphone dyes. The structure of a typical dye Remazol Red B is shown below;

These dyes may be represented by the general formula.



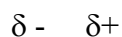
Where D is the colour-forming part and contains one or more solubilising groups.

In this form of the dye, the sulphone group induces polarization of the aliphatic chain attached to it, by which the  $\alpha$  carbon atom in the sulphone group has an electron restraining effect and the carbon atom in the beta position gains a positive charge: -

The electrons belonging to the hydrogen atoms linked to the  $\alpha$  carbon atom are nearer the croton atom than the hydrogen atoms. However, the electron in the neighborhood of the carbon is likely to separate as an anion. Both these tendencies favor the following reaction in an alkaline medium: -

This reaction takes place almost immediately on addition of an alkali to a solution of the original dye in water.

The vinyl sulphone group ( $-SO_2-CH = CH_2$ ) shows strong polarization caused by the siphoned ( $-SO_2$ ) group: -



This activated double bond can then react with water, alcohols and cellulose, forming ethers by the addition reaction: -



(OH<sup>-</sup>)

In the dyeing of cellulose with vinyl sulphone dyes, the reaction with cellulose is always accompanied by reaction with water with the formation of hydroxy ethyl sulphone dye D-SO<sub>2</sub>-CH<sub>2</sub> CH<sub>2</sub>-OH. Which then cannot react with cellulose.

Both the reactions (with fibre and with Water) are catalyzed by alkali. Thus alkali is required in the dyeing of cellulose with these reactive dyes for converting the sulphatoethyl sulphone dye to vinyl sulphone dye with the cellulosic fibre (in the first case, alkali is consumed, while in the other, alkali acts only as a catalyst).

The hydroxyethyl sulphone dye (the reaction product of tri vinyl sulphone dye and water) cannot react with cellulose 81 has very low affinity for cellulose.

In neutral solutions, the sulphatoethyl sulphone dyes 4 marketed) do not undergo any chemical reaction; the aquarius dye solution may even be boiled without the risk of losing reactivity by the formation of the hydroxy ethyl sulphone for of the dye.

## **Exhaust dyeing**

According to fixation rates, Remazol dyes fall into three affinity groups, the first one showing the lowest and the third, the highest. Hence the dyes belonging to the second or group should be selected for exhaust dyeing. Since these dyes have moderate reactivity (this lies between that of monochloro and dichlorotriazine reactive dyes), their optimum fixation temperature is 40<sup>o</sup> to 55<sup>o</sup>C , except for the turquoise dye, for which it is 80<sup>o</sup>C. The dyeing may be classified as follows —

### **(1) Dyeing at 40<sup>o</sup>C**

This is the standard method for dyeing on a jigger and for dyeing of unmercerized cotton in package dyeing and winch beck machines.

### **2) Dyeing at 55<sup>o</sup>C**

Mercerized cotton and viscose rayon show greater absorption of Remazol dyes, and hence to get better leveling results, a higher temperature is chosen (the substantivity decreases with increasing temperature).

### **(3) Dyeing at 80<sup>o</sup>C**

Turquoise blue and green dyes are best dyed at this temperature. A mixture of soda ash and caustic soda or trisodium phosphate only has been recommended as the alkali in the dyeing of these dyes. For the exhaustion purposes 50 g/l of common salt or Glauber's salt is commended. In the case of unmercerized cotton in package dyeing or winch beck dyeing 80 g/l of common salt considerably increased the colour yield especially in dark shades.

If uneven dyeing is noticed after the dyeing process (especially fixation) is over, it is not possible to correct this faultily dyed material; the dyeing has to be stripped and

redeemed. Therefore the production of dyeing involves the control of temperature and addition of alkali to effect fixation (reaction of the dye with the fibre).

However, in the case of package dyeing and winch dyeing the 'all-in' method is recommended. Thus the dyeing (circulation of the liquor through the package or working of the material in the liquor contained in the winch) may be started with the liquor containing the dye, salt and the required amount of alkali at the room temperature and then gradually raising the temperature, during dyeing and continuing the dyeing till the required depth is obtained. When mercerized cotton or rayon materials are dyed, the sequence may be slightly changed. In this case, the dyeing may be stained in a liquor containing the dye and salt only (in the absence of alkali) at 40°C, the required amount of alkali (trisodium phosphate) added after 20 minutes, the dyeing continued at this temperature for another 20 minutes, the temperature gradually raised to 60°C and completing the dyeing at this temperature. Since the fixation will not take place fully at 40°C, the initial dyeing will be slow, ensuring the production of even dyeing.

The amounts of salt and trisodium phosphate depend on the depth of shade dyed. For example, they vary from 50% salt and 5% trisodium phosphate (for shades of up to 2%) to 120% salt 15% trisodium phosphates (for shades of 5% and higher) for unperceived cotton materials. Half of these quantities are enough for dyeing mercerized cotton or viscose rayon materials.

A typical process of dyeing of cellulosic fibre packages is given below: -

## **Scouring**

This is done by circulating a solution containing 2% acetic acid (56%) and 0.25% anionic wetting agent at 60°C for 20 minutes keeping a liquor ratio of 8:1 to 12: 1. The material is then washed with hot water.

If an alkaline scouring is necessary, the residual alkali (after washing) should be neutralized and then the add wailed completely.



## **Dyeing**

The dyebath is set at 28°C with 1% sodium hexameta phosphate (sequestering agent), and 25 to 50% common salt or Glauber's salt (these additions may be done during the filling of the machine). The material is entered and the liquor circulated once. Over the next circulating cycle, the dye (predissolved in ten times its weight of hot or boiling water) is added and the liquor circulated once at 28°C. During the next cycle, 8 to 15% crystalline trisodium phosphate or 8.4 to 6.5% an-hydrous trisodium phosphate is added and the circulation continued at 28°C. (Since boiling is needed to dissolve trisodium phosphate in a small amount of water, ice may be used to cool the trisodium phosphate solution to 28°C: otherwise the dye may react with water in the tank itself due to high temperature conditions prevailing on the addition of boiling phosphate solution. The temperature is raised at the rate of 1°C/min; while continuing the circulation of the dye liquor. When a temperature of about 43°C is reached 25 to 50% common salt or Glauber's salt is added without interrupting the temperature rise. The heating is continued till a temperature of 60° C is reached. The dyeing is continued at this temperature for 45 to 60 minutes. The bath is dropped and the dyed material washed with warm water (about 50° C.

If a lighter shade is produced, cooling with a heat exchanger cools the dyebath to 50° C by both dropping one-fourth of the bath and filling with cold water. The required amounts of the dye is added, and the dyeing continued for 20 minutes at 50° C. If large amounts of the dye are needed to be added, the temperature of the dye liquor should be raised to 60°C and dyeing continued at this temperature and then the bath is dropped.

## **Rinsing and soaping**

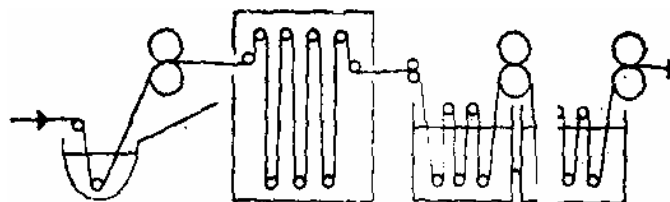
After rinsing the dyeing carried out with warm water (50°C) until clear soaping is carried out with liquor containing 1% sodium hexametaphosphate and 0.25% nonionic detergent at about 93° C. Washed with hot water, acidified with 0.25% acetic acid (56%) at 50°C and rinsed.

The manufacturers for the exhaust dyeing of cellulosic fibre materials recommend the following Remazol dyes: —

- Remazol Brilliant Yellow 7GL: This is the brightest of all Remazol yellow dyes and may be used for producing green combinations at all liquor ratios. However, it does not build up appreciably beyond 2% at a liquor ratio of 20: 1
- Remazol Brilliant Yellow CL: This is an all-Remazol greenish yellow dye and may be exhausted at all liquor ratios; it is not as economical as Remazol Yellow OW or Yellow OR.
- Remazol Yellow OW This has excellent level dyeing properties at all liquor ratios. The shades produced with this dye have good fastness properties. It may be used in all cases except where a greener yellow is needed.
- Remazol Golden Yellow GA: This has very good leveling properties at all liquor ratios and produces reddish yellow shades.
- Remazol Yellow RTN: This metallized dye shows superior fastness to other Remazol dyes, including chlorine fastness. It produces level shades at all liquor ratios.
- Remazol Brilliant Orange Y: This dye is the brightest yellowish orange dye, which can be exhaust-dyed at liquor ratios.
- Remazol Brilliant Orange 3R: This reddish orange dye produces level shades at all liquor ratios -
- Remazol Scarlet 30 This dye produces bright scarlet shades and may be exhaust-dyed at all liquor ratios.
- Remazol Brilliant Red FB: This dye also can be d at all liquor ratios and is more economical than R Brilliant Red BR.

## **Two-bath dyeing of cellulosic fabrics with vinyl sulphone reactive dyes**

These processes are considerably different from one-processes. Since in two-bath processes, the dyes are padded in the absence of alkali, the pad baths are extremely stable. Most of the Remazol dyes are soluble in the absence of alkali at a dye concentration of 100 g/liter and this stability of solutions is practically unlimited regardless of temperature. An additional advantage is the increased dyestuff fixation (about 20%) compare with the one-bath process. However, there is ~ tendency of migration during intermediate drying since the dye has low affinity. The addition of thickening agent and of salts are some means to minimize the migration tendency of the dyes. Reduction of pickup (60%) and creation of a steam atmosphere during the initial part of the drying process are the other means of reducing migration. This may be done by reclining or completely eliminating the air convection in the first one or two compartments of a hot flue dryer. The antimigration effect is increased when the temperature of the pad liquor is raised to 65° to 78° C. Some two-bath sequences are shown in following figures: -



### **Two-bath-pad-roller vat process of dyeing Remazol dyes**

The two-bath pad-bath method involves padding of the cloth with the dye solution, drying and again padding with a cold solution of alkali and salt and batching the material. A salt concentration of 200 to 250 g/liter is required for avoiding the migration of the dyestuff into the alkali pad bath. This method produces the best colour yield among all

Remazol dyeing methods. Where steam range is not available, this method is the ideal one.

Wet fixation requires a passage of the, padded and dried material through a hot solution ( $95^{\circ}$  to  $100^{\circ}\text{C}$ ) containing salt and caustic soda. At a concentration of 50 ml/liter of  $38^{\circ}$  Be caustic soda solution, the fixing time is 3 to 5 sec. at  $95^{\circ}$  to  $100^{\circ}\text{C}$ . The developing bath should be provided with direct heating means.

The two-bath steam process is the most important one for dyeing Remazol dyes. In the case of mercerized cotton fabrics, the alkali pad bath should contain 200 to 250 g/liter salt and 20 milliliter/liter  $38^{\circ}$  Be caustic soda solution. Steaming time is 30-35 sec. where the machinery used involves longer steaming times; the concentration of caustic soda in the alkali pad bath should be reduced. Thus a steaming time of 60 sec. requires about 10 to 12 milliliter/liter  $38^{\circ}$  Be caustic soda solution. On the other hand, steaming times of less than 20 to 25 sec. require the alkali pad bath of different concentrations. Thus a steaming time of 5 to 7 sec. requires the alkali pad bath containing common salt (180 g/liter soda ash (150 g/liter), potash (50 g/liter) and  $38^{\circ}$  Be caustic soda (80 ml/liter). For unmercerized cotton, the alkali pad bath should contain common salt (300 g/liter) and  $38^{\circ}$  Be caustic soda solution (15 milliliter) and steaming may be done for 60 sec. This modification produces 10 to 20% deeper shades than when 20-mil/ liter  $38^{\circ}$  Be caustic soda solution was used and the steaming carried out for 30 sec.

In a Japanese process,  $44^{\circ}$  Be sodium silicate (with  $\text{Na}_2\text{O} : \text{SiO}_2 = 1 : 2.6$ ) replaces common salt and caustic soda chemical pad bath. The steaming is done at  $105^{\circ}\text{C}$  for 30 sec. This modification is reported to have reduced the migration tendency in the chemical pad to such an extent that light and deep shades through the same chemical pad solution without the danger of staining are produced. This method is suitable for dyeing small lots.

## **After-treatment**

Two factors are important during the after-treatment of Remazol dyeing. The dyeing should not be soaped at the boil under alkaline conditions. Neutralizing with acetic acid before soaping ensures this. The unfixed (hydrolyzed) dye is removed by boiling with a detergent solution at the boil.

It is important to note that the substantivity of the unfixed dye is reduced at higher temperatures and at the boil, the dye has practically no affinity for the fibre and the loosely held dye rapidly diffuses out. If this dye is removed completely, it is not necessary to treat the dyeing with a cationic dye-fixing agent to achieve the optimum perspiration and water fastness.

If the boiling after-treatment is carried out under alkaline conditions, some amount of the dye already fixed (reacted with the fibre) is separated by the rupture of the dye-fibre bond, since this bond is not stable to alkali especially at the boil.

When sodium silicate is used as the alkali for fixing the dye, neutralization with acetic acid should not be done. If it is upraised insoluble silica acid may get deposited in the fibre reducing a harsh feel. In this case, an overflow rinsing with water should be given before the boiling after-treatment. Sodium silicate is more easily washed off than caustic soda). Sodium hexametaphosphate 2 g/liter is to be added to the boiling after-treatment bath.

# Types of Dyeing Methods

## 1. Pad-batch process

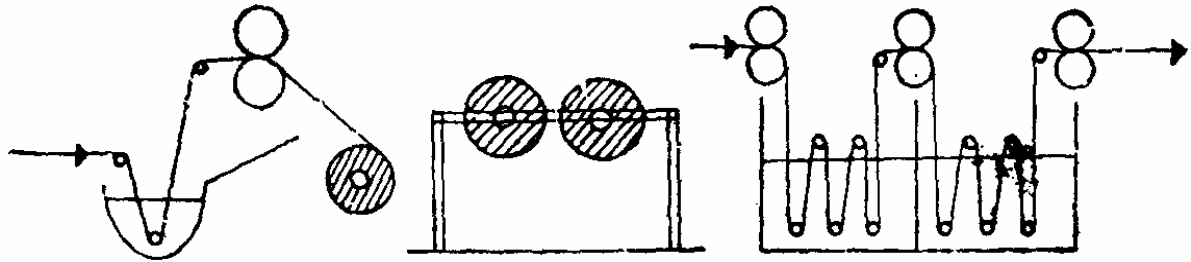
In this process the cellulosic fibre fabric is padded with a reactive dye solution in the presence of an alkali, usually sodium bicarbonate stored in the wet condition for a prescribed period and finally washed off. Depending on the temperature dulling storing two sequences are employed

(1) Pad (alkali) Batch (cold) process.

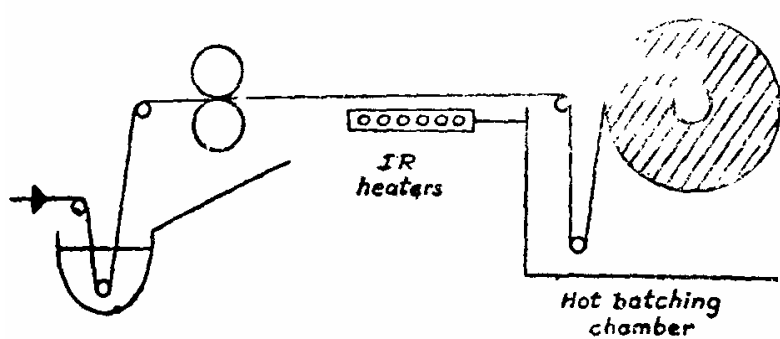
(2) Pad (alkali) - Batch (warm or hot) process.

In the first sequence the padded cloth is covered with a polyethylene sheet (to prevent evaporation of water) and stored for two hours and finally washed. The second one is similar to the first sequence, except that a milder alkali is used in the pad bath and hot batching is carried out. The machinery Deeded in the two sequences are shown in Figures.

Soda ash, sodium meta silicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) and caustic soda may be used depending on the depth of shade dyed. Because of the high reactivity of cold brand reactive dyes with these alkalis, a short fixation time is enough. However, the pad Liquor (containing the dye and the alkali) is stable only for a short time. Hence the dye and alkali solutions should be prepared separately and mixed immediately before use. With these alkalis giving pH values of 10.5 to 11 (soda ash), 11 to 12 (sodium metasilicate) and 12 to 12.5 (caustic soda), the fixation time is 1 to 4 hours at 20 to 30°C for cold brand dyes and the pad bath stability is 5 to 30 mm. When soda ash and sodium bicarbonate (3:1) mixture (pH 10) is used, the stability increases (20 to 60 mm.), but the fixation time is prolonged (4 to 24 hours). If bicarbonate alone used (pH 8), the stability is 30 mm. to 2 hours with time of 8 to 48 hours.



### Pad (alkali)-Batch (cold) sequence of dyeing reactive dyes



### Pad (alkali) – Batch (hot) - Process

In the case of pad-hot batch method, sodium bicarbonate (pH 8) and soda ash (pH 11) are used for cold brand and brand dyes respectively (batching temperatures of 50<sup>0</sup> to and 75<sup>0</sup> to 95<sup>0</sup> C and the fixation time is 1 to 3 hours the bath stability is 30 mm. to 2 hours.

In the case of deeper shades being dyed, sodium silicate ( $\text{Na}_2\text{O}:\text{SiO}_2 = 1:1$ ) is preferred due to the unparsed by the solubility of dye and soda ash and the rate fixation. Urea (50 to 200 g/l) may be added to improve dye solubility.

In actual practice, properly prepared fabric is padded the liquor containing the cold brand dye and the suitable at 200 to 30°C (the lower temperature is preferred on the grounds of bath stability). The temperature should be kept constant to avoid variation in shade, especially when mixtures of dyes of different reactivity are dyed. High padding speeds

with adequate wetting-out of the fabric are preferred. Sm8 volume pad troughs are recommended.

After padding, the batches are wrapped in polyethylene sheet and stored at room temperature. They may be over-night, if necessary. During the storage period, they may be kept slowly rotating to prevent seepage of dye liquor. However, with a good expression of the padding mangle moderate size batches, the danger of seepage is small.

When the required batching time has passed, the cloth is bed in a rope washing machine. Under the practical conditions of washing, the unfixed reactive dye is removed in two sates, both depending on temperature. Initially the dye bleeds rapidly and the rate of removal is detonated by the removal d the coloured wash liquor. In the second stage, which is more important for high-affinity dyes, the amount of dye washed is small and takes longer time.

In the pad-hot batch method, (Syetema method) the properly prepared fabric is padded with the dye and alkali, passed between infrared heaters to preheat the padded fabric to 50<sup>0</sup> to 95<sup>0</sup>C arid then batched on a large diameter roller in a hot chamber. The batching is done under controlled conditions of temperature and humidity for a sufficient time to ensure diffusion and fixation of the dye in the fibre. During this period the batch is kept slowly rotating to avoid seepage of the dye liquor. The cloth is then removed for washing.



## 2. Continuous Processes

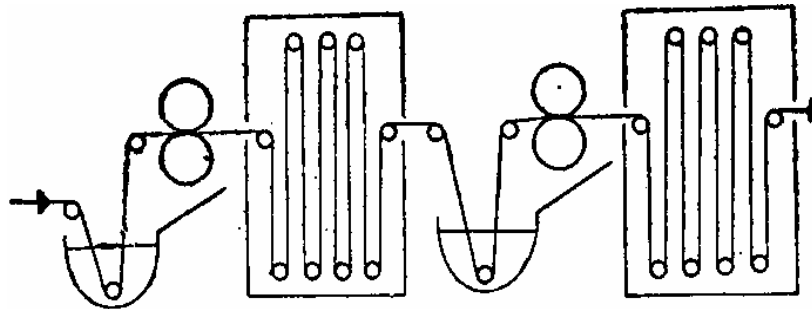
The reaction between the cellulosic fibre and the reactive dye takes place in the presence of water and alkali in a short time at elevated temperatures. The rate of reaction is further increased at high pH values. This is the basis of many continuous dyeing methods. Depending on the reactivity of the dye two processes—single padding and double padding—are available. In the former, the pad liquor contains the dye and the alkali, which does not hydrolyze the dye at room temperature, but promotes fixation at a higher temperature. For cold brand reactive dyes sodium bicarbonate is the preferred alkali. Which on beating produces sodium carbonate the streamer alkali. For hot brand reactive dyes, sodium carbonate is added to the pad liquor. The following sequences are possible –

- a) Pad (bicarbonate) - Dry process.
- b) Pad (alkali)-Dry-steam process with sodium bicarbonate or carbonate as the alkali.
- c) Pad (bicarbonate) — steam process.
- d) Pad (alkali, urea) — Dry-Cure Bake process with sodium bicarbonate or carbonate as the alkali.

In the double padding process the fabric is first padded with the dye solution in the absence of an alkali and with or without drying it is re-padded with a solution of caustic soda ~ common salt and finally steamed to fix the dye.

## Single padding processes

Essentially the process consists in padding the cloth with liquor containing the reactive dye, alkali (usually sodium bicarbonate), Glauber's salt and sodium alginate (migration inhibitor) and a wetting agent and then drying. In this case the drawing has to be done slowly; otherwise, precipitation of the dye due to quick removal of water may take place leading to lower colour values.



The fixation of the dyestuff falls with increasing depth of shade being dyed, because of the precipitation of the dye-taking place during dyeing. This can be avoided by the following ways -

- (a) By adjusting the drying conditions (this may not always be possible with hot flue systems).
- (b) By injecting steam into the drier,
- (c) By adding a non-volatile solvent to 'the pad liquor, and
- (d) By using an alternative alkali.

When steam is introduced (3.5 g of steam/min./ 100 liters of oven capacity) into the drier, the percent fixation increases tremendously. Thus for Portion Brilliant Yellow

60S, Yellow RS and Brilliant Orange GS on cotton fabrics, the percent fixation values for drying at 105<sup>0</sup>C without steam are 40, 46 and 62 respectively, while the corresponding values in the presence of steam are 84, 76 and 73 respectively. When heated at 150<sup>0</sup>C without steam, the fixation values are 58, 63 and 64 and with steam, 90, 85 and 76 respectively. Similar effect of introduction of clean in the driers is seen in the case of dyeing of viscose rayon with relative dyes.

The introduction of steam in the drier reduces the rate of drying of the cloth, giving longer reaction times. Secondly steam injection increases the fixation rate owing to higher wet-bulb temperature. Steam baking gives still higher fixation with reduced reaction times.

### **Pad (bicarbonate, urea) — Dry process**

In this case a non-volatile solvent is added to the pad bath. Urea has been found to be the most effective agent and produces marked improvement, especially when deep shades are dyed. This is due (1) to a lower rate of evaporation of water which itself is due to the elevation of the boiling point, of water (2) to a higher cloth temperature and (3) to the solvent action of urea.

### **Use of soda ash**

When the drying rate is very high, the cloth temperature is too low and the reaction time too short for efficient fixation of the dye with sodium bicarbonate, which itself might not decompose (into sodium carbonate) due to non-availability of water and hence a low pH may be maintained. In such cases sodium bicarbonate may be replaced by an equivalent quantity of sodium carbonate when satisfactory fixation is achieved. However, this can be done at the expense of pad liquor stability.

## **Cylinder drying**

In steam-heated cylinder drying units, the drying of the cloth is achieved by contact with a hot metal surface. Which is more efficient than hot air drying. Cylinder driers give Bo quicker fixation and higher fixation. Generally, for cold brand reactive dyes, cylinders operating at 103<sup>0</sup> to 105<sup>0</sup>C with a drying time of 60 to 70 sec. are satisfactory.

## **Hot brand dyes in pad-dry process**

Since hot brand reactive dyes are less reactive and have, higher stability to I<sub>c</sub> alkaline solution than cold brand reactive dyes. They are less suitable for application by pad (alkali) -dry process. However, when they are dyed by this method, sodium carbonate may be used as the alkali instead of sodium bicarbonate. Because of the lower reactivity of these dye pad (alkali, urea) - dry process is more suitable. In addition, a Sort baking treatment (at 110° C to 125° C for 3 to 5 minutes) is helpful in increasing the fixation.

In the case of pad (alkali) steam process, higher cloth temperatures are attained, resulting in rapid dye fixation. Also the presence of steam does not allow quick drying to take place. The alkali used in this case is soda ash.

## **Double padding process**

In one process, the fabric is padded with the dye solution 3rd repadded (with or without intermediate drying) with an alkali solution containing a high concentration of salt to minimize bleeding of the dye from the cloth into the alkali bath: and then steamed. There are two variations of the process depending on whether an intermediate drying is done or not. In wet-on-wet system the intermediate drying is omitted while it is carded out in wet-on-dry process. The former process is suitable for dyeing pale shades, where bleeding of the dye in the alkali bath is negligible. In padding mangles with small liquor space (5 to 10 liters) short volume liquors are rapidly taken up

by the fabric being padded and the constant rapid replacement of the pad liquor minimizes the extent of tailing effects. Further, the wastage of the residual liquor at the end of padding is low. The pad troughs should be fed with the solutions from storage - tanks kept at proper temperatures (room temperature for cold brand dyes and 40° C to 50<sup>0</sup>C for hot brand dyes).

## **Jigger dyeing**

A wide range of cotton, linen and viscose rayon fabrics can be dyed with reactive dyes in jiggers. The operation in the cold eliminates the problems usually associated with jigger dyeing by raising the temperature during dyeing with other classes of dyes. However, certain tightly woven or dense materials or fabrics woven from highly twisted yarns are difficult to dye by the cold dyeing method in jiggers. Raising the temperature or pre-padding followed by jigger development improves the dyeing process in these cases.

In all batch wise dyeing methods, the fixation reaction is accompanied by the hydrolysis of the reactive dye to various extents. In jigger dyeing each part of the fabric is presented with fresh dye liquor intermittently, at a rate determined by the size of the batch and the speed of the machine. Thus the opportunity for the fixation reaction is decreased when large batches are dyed or when the jigger is run slowly (longer ending times). Due to the intermittent nature of dyeing, the dyebath stability. (Reactivity of the dye) in the alkaline bath has to be taken into account.

It may be possible to shorten the dyeing time by setting the dye bath initially with all the required salt, and then adding the pre-dissolved alkali over two ends, especially while dyeing low affinity dyes.

## **Pad-Jig method**

With heavy, tightly woven materials, good penetration of the dye in the materials may not be achieved in jigger dyeing. In such cases, the cloth may be pre-padded at 30<sup>0</sup> to 50<sup>0</sup> C with a solution of the dye containing 1 to 2 g/l of nonionic surfactant like Lissipol N.

The wet padded cloth is then run on the jigger set with the required amount of the alkali and common salt. The amounts of alkali (soda ash or caustic soda). And of common salt, the temperature and time of dyeing are same as those recommended for batch wise dyeing of reactive dyes. In certain cases (e.g., Procion Rubine B and Blue 3R on viscose rayon) batching for 1 hour between padding and jigger fixation increases the colour value.

When the padding conditions are unsatisfactory, the padded cloth may be given two ends in the jigger containing the salt only and then adding, the alkali. This levels out any initial uneven padding results.

# **Metal ions and their associated problems in the textile processing**

## **Introduction**

In the textile-processing sector "to sequester" means to remove or render innocuous disturbing metal ions coming from various sources. It is well-known fact that the presence of different metal ions in the various processing baths interferes with treatment chemicals and dyes, thereby hampering the quality and reproducibility of the processed textile material. In the emerging business scenario customer satisfaction occupies a pivotal point in determining the success of any produced. Evidently, to attain the quality of the processed goods it is desirable to apply sequestrants at the different up stream process when necessary.

## **Sources of metal ions**

The metal ions incorporated in the various states of the textile processing different sources are as follows:

### **Water**

Water is an indispensable part of processing textile in the wet condition and so the quality of the water used in the textile finishing industry plays a very significant role. The harmful metal ions ( $\text{Ca}^2$ ,  $\text{Mg}^2$ ,  $\text{Fe}^3$ , etc) present in the processing water not only necessitates the undesirable and expensive usage of increased quantities of the textile auxiliaries and dyes, but also hard water interferes with the finishing processes as well causing deposits on the textile substrates, on the equipments, pipelines etc. resulting in poor quality of the process fabric, and or the other various difficult. The most prominent among them are:

- Formation of insoluble earth alkali carbonates, hydroxides, and phosphates in the alkaline medium,
- Formation of insoluble earth alkali silicates in the peroxide bleached fabric,

- Formation of insoluble time soaps etc.
- Deposition of sludge and scales on the machinery, goods, and rollers causing various problems.

The other problems generally faced are blocking of peroxide stabilizer by excess calcium and causing precipitation of magnesium ions resulting in poorer peroxide stability. Earth alkalis act as emulsion breaker, thus preventing the removal of oils and fats. Lower solubility of dyestuffs, formation of insoluble salts with optical brighteners change of shade of sensitive dyes, imperilment in the removal of hydrolyzed dyes are some other common problems.

### **Origin of cotton**

Depending on its origin, raw cotton can exhibit widely different contents of alkali earth metals, e.g.

Ca – 500-1000 mg/kg

Mg – 300 – 600, mg/kg

Fe – 2-6 mg/kg etc.

These values mainly depend on the salts that are absorbed by the plants. All these sources of alkaline earth metals make it more and more difficult for the processor to guarantee a uniform, reproducible quality of the fabric, ready for dyeing, printing and finishing. At a liquor ratio of 1:10 the gray cotton substrate alone can introduce 25<sup>0</sup> – 30<sup>0</sup> of German hardness into the preparation bath.

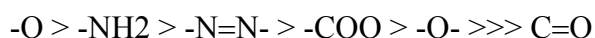
### **Common salt**

A huge amount of contaminating metal ions may enter into the processing system through the addition of common salt only. This is because for a larger variety of dyes the addition of common salt is essential to facilitate proper exhaustion of the dye.



## Use of sequestrates

The various discrepancies faced by the processor as mentioned above could be solved by using chemicals that react preferentially with the metal ion, effectively preventing it from interfering with the mainstream reaction process. Such chemicals are known as sequestering agents. Sequestering agents prevent metal ions from performing detrimental action. They work by mechanism of complex formation and the resulting complex, remains soluble and innocuous under the condition of processing. The most useful donating atoms are nitrogen in the form of amines or substituted amines and oxygen in the form of carbonyl, phosphate or ionized hydroxy groups. Van Viter and Formalities have shown the important co-coordinating functions for their affinity towards metal ions in the following order: -



Sequestering agents are probably used rather indiscriminately by most of the tactile processors in amounts far in excess of the stoichiometric quantities required by the particular set of conditions. Instructions often simply state the addition of 0.5-2 g/l of a suitable sequestering agent. Whilst using sequestering agents are strictly governed by various structural factors and physicochemical factors that among other things determine the hierarchy of efficacy. Various structural factors which influence use bonding strength between the chelating and metal ion are, number of chelate rings, strength of the bond between donor group of chelate and metal ion, size of metal ion, charge of the metal ion, etc.

So a discriminating approach can be adopted while choosing the right agent, it is better to consider in detail the reaction scheme and conditions meaning correlation. Various factors like the type of particular chelating agent and its concentration, metal ion and its concentration, presence of other metal ions, total ionic strength, PH of the dilution temperature affect the stability of the metal-chelate complex etc.

A generalized Scheme of complex action reaction may be as follows:

**Sequestering agent + Metal ion → Chelsea complex**

Stability of the complex is generally **expressed** in terms of its stability constant, which is the logarithm of the equilibrium constant of the reaction shown above. A high stability constant indicates a high sequestering effect. A prime requirement is the formation of the stable ring with the metal ion. The highest stability resulting from five and six member rings.

Sequestering agents which exhibit commercial value in textile processing are as following:

1. Amino polycarboxylates
2. Phosphates, mainly inorganic
3. Hydroxyl carboxylates
4. Poly carboxylates
5. Phosphonates

Different products offer various over alls sequestering power as well as different specific sequestering power for individual metals.

**Amino polycarboxylates:** These are powerful chelating agents, the most common is undoubtedly ethylene diamine tetra acetic acid generally known as EDTA, DPTA, diethylenetriamine penta acetic acid and nitrilotriacetic acid (NTA) and their sodium salts. They are used largely in heavy-duty industrial detergents. They show strong sequestering capacity within the optimum pH range and are fairly stable to acidic and alkaline condition and over sufficient temperature range. They cannot help in detergency through soil suspension. The heavy metals like Pb, As, and Cd are easily chelated by these compounds. The order of stability of metal chelates in terms of logarithm of equilibrium constants for the amino poly carboxylates are as follows:

**Polyphosphates:** The most widely used of this series are sodium hexametaphosphates, potassium pyrophosphates and sodium tripoly-phosphates. They have very good sequestering capacity of calcium and magnesium in the pH range 6-12, and make a good contribution to detergency through soil dispersion and suspension. These are relatively less effective as preparation sequestrates for alkaline scouring and bleaching of cotton. They do not demetallize metal containing dyes so they can be used as reactive bath sequestrants. Polyphosphates are some times formulated into products used for the acid demineralization of griegie cotton. These types of sequestrants show an inhibition effect and so are used during scale formation in presence of high concentrations of electrolytes.

**Hydroxy carboxylates:** The hydroxy carboxylic acids provide a range of sequestering agents of which the best known is citric acid, tartaric acid and gluconic acid and their sodium salts. They have a true chelating action only above pH 12, forming very strong complexes with iron, copper and other heavy metal ions. Their optimum pH of activity is 13-14.

**Polycarboxylates:** these compounds have a high sequestering capacity of complex and disperse calcium and magnesium ions. The most common example of this type is the polyacrylates. The commercially available products vary in chain lengths. Products in the lower molecular weight range are most useful in weakly acid or alkaline pH. These products show good dyestuff solubilising and dispersing properties. Sometimes used for dissolving and soaping off of reactive dyes.

Products of the medium molecular weight range are useful in scouring and bleaching operation for their soil suspension properties. The higher molecular weight products impart viscosity and lubricity in dyebath to reduce abrasion and rope marks in the piece form.

## **Process of demineralization in different textile processing using sequestrants**

### **Acidic demineralization**

Nowadays acid demineralization is an essential part of the processing of cotton goods. Due to presence of alkaline earth metal impurities within the cotton fabric the peroxide bleach on grieger material carriers with it the risk of a catalytic damage. Moreover a high alkaline earth metal content of the fabric may also cause problems in pretreatment and subsequent dyeing and finishing process. To eliminate these harmful catalysts the protonic agents are applied which ionize the metal. This product irreversibly sequesters the metal, now ionized in an aqueous solution, so that it can finally be eliminated in the final washing off treatment.

Various leading textile auxiliary manufacture have come in the market with their protonic demineralization kit.

The acid demineralizing agents generally show the following properties:

1. Strong acid sequestering agent with high pH buffer capacity.
2. Very good sequestering capacity for hardness and heavy metals.
3. After neutralization in the subsequent process these agents keep their sequestering properties under alkaline condition also.
4. In discontinuous process one bath-two step demineralization- peroxide bleach these products can be used as demineralization agent as well as a stabilizer,
5. These products are not generally steam volatile.

Generally an, acid demineralization is carried out at pH level of 2-2.5. These products are based on copolymers of sugar and polyacrylates blended with organic and inorganic buffering systems or synergistic mixture of different phosphonates etc. These are generally stable to acids, alkalis, oxidizing and reducing agents.

The favorable results obtained in the processed goods are as follows:  
Catalytic damage or the fabric reduces.

1. Degree of whiteness of treated fabric Increases.
2. Tensile strength of the processed *fabric* retained.
3. DP value of the subsequently finished fabric increased

Acid demineralization of the gray fabric cannot be recommended, since the size present on the gray fabric hinders the removal of metal ions. To overcome this problem the process of combined desizing and demineralization has been developed.

The protonic demineralization is generally preferred for the following processes:

### **Pretreatment for dyeing**

Demineralization – peroxide bleach (1 bath – 2 step)

Peroxide bleach - demineralization, and neutralization,

### **For optical bleach**

Demineralization – Peroxide bleach (OBA), 1 bath – 2 step process

Demineralization – Peroxide bleach (OBA), 2 bath – 2 step process

### **Continuous bleaching**

Used for continues demineralization and bleaching.

### **Bleaching with peroxide**

To remove the alkaline earth metals present in the bath, chelating agents stable to alkaline pH are added to the bath to prevent undesired precipitation and catalytic damage to the fabrics due to the catalytic dissociation of the  $H_2O_2$  and the resultant fabric will be of better whiteness and tensile strength. Efficacy of the detergents in the scouring and the bleaching bath are also improved

## **Application of sequestrates in the dye bath, OBA bath, rinsing operation**

Chelating agents added to the dyebath and during soaping treatments. It is seen that the presence of alkaline earth metals sometimes have a detrimental effect on the shade build-up, often the problems like tonal change, precipitation of the dyestuffs, unlevelled dyeing, reduced colour yield, improper solidity of the shades, dulling of the shades and poor wet fastness, etc. are faced by the dyers.

Traces of certain metal ions, particularly in solutions may cause quench, rig or fluorescence even in very small amounts, especially due to the presence of Cu and Fe ions in the treatment bath, and lowering of the whiteness index occurs, under these conditions addition of a sequestering agent in the treatment bath is really helpful.

Calcium ions impair the removal of hydrolyzed dyes when dyed with reactive dye, thus having negative effects on the wet fastness properties. Cotton dyed with reactive dyes accumulates calcium ions. For this reason, soft water should be used if possible for dyeing and for entire after treatment. The presence of calcium ion in the soaping bath deteriorates the removal of hydrolyzed dyes, so to achieve *adequate* fastness properties of the dyed material, the number of rinsing *and* soaping baths in sequence along with the temperature of these baths have to be increased. By using selected polyacrylate based sequestrants good wet fastness properties can be achieved even in the presence of calcium ions. So after the dyebath drain, thorough rinsing at higher temperatures along with a sequestering agent is very much helpful to improve the efficacy of the soaping process. Now a days leading textile auxiliary manufacturers introducing their novel after soaping ping formulations for different dyes and also the dye bath stabilizers in which the use of sequestrants is a must.

## **Hidden threats of Bicarbonates in Reactive Dyeing**

The reactive dye segment is growing at the expense of other dye types, such as vat, direct and sulphur dyes

### **Reactive coloration**

Developments have become necessary, as consumer demand has focused on

1. Fastness properties
2. Ease of application
3. Economy and, not least, the environment
4. Preparation
5. Dyeing, including a new approach to dyestuff compatibility
6. Washing-off hydrolyzed dye
7. Fastness

### **Practical considerations**

#### **Hardness and bicarbonate**

Successful reactive dyeing will depend on many factors, including (obviously) the choice of reactive dyes. Other important factors will be:

1. The choice of supplier of those dyes (and therefore quality).
2. The Choice of auxiliaries, and the quality of those auxiliaries (and therefore the supplier).
3. The choice of processing and dyeing machinery.



4. The education and training of the workforce.

For a given supply of reactive dye, on a particular dyeing machine and with a given set of operatives, it is necessary to control the dyebath in two particular respects.

1. Hardness / metal contamination.
2. Bicarbonate.

### **Consequences of "uncontrolled dyebath contamination"**

1. Premature reactive dye fixation before migration (possible unlevelled dyeing)
2. Premature reactive dye hydrolysis before fixation (possibly resulting in poor fastness, loss of dyestuff yield and reduced economy of recipe)
3. Poor shade reproducibility (lower productivity)
4. Lost time.

### **Hardness in the dyebath: The safety limit**

It is internationally recognized that the maximum degree of hardness permitted in the dyebath for successful dyeing with (and direct) dyes is 3 degrees German (or 60 ppm). This may be taken to be the "safety limit".

However, it is not always readily recognized within the industry that there are four principal sources of potential metal contamination, which can create hardness in the dyebath.

1. Water
2. Cellulose fibre
3. Chemical auxiliaries
4. And the added electrolyte

Therefore, it is necessary to evaluate each of these potential sources of contamination (or hardness) in detail. In our experience, it is the hardness in the cotton and electrolyte; it is the hardness in the cotton and electrolyte, which are often not looked at closely enough.

With the cotton fibre, it is the level of the contamination within the cotton structure itself, rather than simply the level of contamination in the surface, which is important. It is necessary to examine the internal structure of the prepared cotton for residual hardness and other possible impurities.

It is a relatively simple matter to estimate what levels of hardness may be expected from current preparation process and working conditions. It involves measuring the "internal" hardness of prepared substrate in the presence of the highest concentration of electrolyte used at the heavier depths of shade, and in the pertaining production water supplied to the dye house. The test produce can be simplified as follows.

### **Test procedure**

1. Place prepared cotton in water from production at the same liquor to goods ratio as that used in production for dyeing.
2. Cover the beaker with a glass evaporating dish (or aluminum foil) and heat to 98 °C for 15 mins.
3. Cool to room temperature and add 90 g/l of electrolyte.
4. Call this solution X
5. Solution X represents the "blank dyebath" (dyebath without dye).
6. Measure the amount of hardness in solution X, and the amount of Chromaquest PDC necessary to ensure zero hardness (0 degree German)

## **The "Hidden bicarbonate threat" to successful reactive dyeing**

### **Origin of bicarbonate in dye house water**

Most water softening treatments are based on an ion-exchange column. This is a series of layers of zeolite resins, which absorb heavy, and alkaline earth, metal ions. The system is almost like a series of molecular sieves.

The production of soda ash from heating solutions containing sodium bicarbonate leads to the formation of an alkaline buffer system (i.e. sodium bicarbonate + sodium carbonate). This means that water containing sodium bicarbonate prevents a risk of the formation of alkali in a reactive dyeing system, before alkali is actually required.

### **Measuring bicarbonate in the dyebath**

It is a relatively simple matter to determine whether or not bicarbonate is present in the dyebath. This can be done quite easily by measuring the pH before and after boiling a sample of the water. The beaker of water should be covered to prevent losses due to evaporation.

### **Why is the increasing pH phenomenon important?**

A reactive dye's ability to dye level is governed by its migration potential, i.e. the ability the dye has to diffuse throughout the fibre matrix, as a function of temperature and time, before fixation or hydrolysis occur. If alkali is present, fixation or hydrolysis will start to develop, stopping and further ability of the dye molecule to diffuse, thereby limiting the leveling power. This can result in unevenness, poor colour yield and poor reproducibility of shade.

### **Controlling bicarbonate in the dyebath**

Repeat the "boiling water" test with, and without, increasing amounts of Chromatch Controller RD-BF until both pH1 and pH2 are controlled in the region 5.5 to 6.5.

Chromatic controller RD-BF is a recently developed unique product.

It can help to "control" the potential dangers, or threats to successful dyeing with 4 functions:

1. Bicarbonate killer
2. Provides robustness to bicarbonate variation
3. Some dispersing properties.
4. Good sequestering power.

In-exchange only removes the cations, but does not remove the bicarbonate anion, which is potentially dangerous to both Reactive and Disperse dyeing. Bicarbonate can cause: unlevelness; loss of dyestuff yield; and poor shade reproducibility.

The amount of bicarbonate in any industrial softened water will vary according to the hardness of the incoming water which itself will vary seasonally with the climate; during each cycle of the ion-exchange column before regeneration; from one shift to another on a given day; from one day to another and in an unpredictable manner.

## ACRYLAMIDE POLYMERS

In the last twenty years, the industrial use of acrylamide polymers has grown enormously. Significant commercial advances have included development of catalytic processes for the preparation of the monomer, introduction of easily handled emulsion polymer, and identification of larger potential uses in enhanced oil recovery. Many other uses for polyacrylamide have been explored. But the principal outlets continue to be in water treatment, mining & paper manufacture.

### Physical properties

Acrylamide  $\text{H}_2\text{C}=\text{CH}.\text{CONH}_2$  (2 propenamide) is a white crystalline solid. the important physical properties of Acrylamide are summarized below:-

Property	Value
<b>Molecular Weight</b>	71.08
Melting Point, °C	84.5±0.3
Vapor Pressure	
<b>Solid Pa (mm Hg)</b>	
25°C	0.9 (0.007)
40°C	4.4 (0.033)
50°C	9.3 (0.070)
<b>Liquid Kpa (mm Hg)</b>	
87°C	0.27 (2.0)
103°C	0.67 (5.0)
136°C	3.3 (25)

Density, g/ml at 30°C	1.122
Optical Properties	
Crystal System	Monoclinic or triclinic
Crystal Habit	Thin tabular or lamellar
Solubilities g/100 ml, Solvent at 30°C	
Acetone	63.1
Benzene	0.346
Chloroform	2.66
Ethanol	86.2
Ethyl acetate	12.6
Methanol	0.0068
Water	215.5
CCl <sub>4</sub>	0.038

## **Polymerization of Acrylamide Monomers**

### **Free radical polymerization**

#### **Polymerization in solution**

Acrylamide polymerizes easily in the presence of free radical initiators to form of chain of structure.

Where n is 20000-300000. In commercial literature copolymers containing atleast 50% acrylamide often designated PAM.

Solution of acrylamide in water polymerizes at moderate temperature under the influence of nearly all free radical sources including peroxide, persulphate, redox couples & azo compounds. These are classical vinyl polymerizations, involving the normal steps of initiations, propagation, chain transfer, mutual termination of pairs of growing chains. Reactions are homogenous throughout and may be carried essentially to completion. Inhibitors, chain transfer agent, temperature changes influence results.

### **Polymerization in the Solid state**

Acrylamide may be polymerized in the solid state through the use of ionizing radiation. Crystals may be irradiated continually during the course of reaction at ca 0-60°C.

The crystalline matrix seems unable to exert any appreciable degree of steric control. Polymer made in the solid state is amorphous and shows no indication of being crystallizable. Polymer chain growth occurs largely at the interface between in compatible monomer & polymer phases.

Crystalline is also polymerize by exposure to UV light. Polymerization occurs on the surface crystalline mass and thus the thickness of the sample is a controlling factor. Post exposure polymerization similar to that with  $\gamma$  rays is observed in the UV system, but the rate is much slower. Polymer made using UV sources have been reported to be highly branched.

### **Commercial Polymerization**

Of the many methods used to make polyacrylamide in the laboratory only a few are useful in the plant. The oldest and still widely used method employs a dilute 8-20% aqueous solution and a conventional azo, peroxy or redox initiator. Batch reactors are common but continuous stirred tanks reactors may be substituted. The method is straight forward for low molecular weight, but very high molecular weight polymer form gels, that arte hard to handle in a typical solution procedure, a solution of polymer in a deaerated water is allowed to react under nitrogen, with a small amount of free radical initiator until conversion to polymer reaches 95-99%. A common reaction time is 4-8

hour. Chain transfer agent example isopropyl alcohol may be present and chelating agents may be used to remove iron or other metals. If the viscosity is not too high the mixture may be stirred throughout. Heat may be removed by external cooling to maintain a constant temperature, often 20-50°C, or reaction may be initiated at low temperature & temperature allowed to rise adiabatically to 60°C or higher.

## **Polymer properties**

### **Properties of solutions**

Polyacrylamide is soluble in water over the entire range of concentration & has no upper and lower temperature limits. An extrapolated theta temperature in water is ca-40°C.

Very dilute filtered solution of polyacrylamide in water contains only individual, unassociated polymer coils. The upper concentration limits for truly particulate solutions varies inversely with chain length. Large sometimes-fibrous aggregates have been observed in diluted aqueous solution of high molecular weight polyacrylamide, even after centrifugation to remove insolubles.

The viscosity of polyacrylamide homopolymer solutions is independent of  $\Phi$ , but that of partially hydrolyzed solutions passes through a maximum at intermediate extent of neutralization. Formaldehyde, hydrazine, ethylene glycol, morpholine are solvents for polyacrylamide. Most other organic liquids are non-solvents.



**Table: Physical properties of Solid Polyacrylamide**

<b>Property</b>	<b>Reported Value</b>
Density, 23°C, g/cm <sup>3</sup>	1.302
Critical surface tension, Nn/m	30-40
Glass transition temperature, °C	153 165 188 194,204
Approximate softening temperature, °C	210

### **Flow Properties**

The observed viscosity of polyacrylamide solutions in water depends not only on concentration, molecular weight, temperature, but also on such variable as shear rate, passed history of solutions, & mechanics of measuring techniques. These complexities make it difficult to assess literature reports and to compare one set of results with another.

At very low shear rates, viscosity is independent of shear rates, but if rate is increased beyond a certain point, viscosity drops markedly at a given temperature, the upper limit of the zero shear range decreases with molecular weight and also with polymer concentration. The point at which shear thickening occurs is thus controlled by the size & no. of polymer coils requires to reach a certain packing density. Solution viscosity increase with molecular weight.

## **Chemical reactivity**

Polyacrylamide undergoes reactions typical of low molecular weight amides, and therefore is useful precursor to a variety of functional derivatives. In some cases, the reaction of polyacrylamide provides more convenient or less expensive route than does co polymerization with functional co monomer. Properties of derivative polymers are usually close to those made by copolymerization. The reaction medium is generally water or water in oil emulsion.

## **Uses**

Water-soluble polymers are used commercially include natural products (gums, polysaccharides, animal protein), derivatives of natural products (cellulose ethers) & wholly synthetic product. The most widely used members of wholly synthetic type are based on acrylamide. Valuable characteristics of polyacrylamide are principally the following: -

Exceptionally high molecular weight is accessible. Because chain length is frequently to product performance, polyacrylamide is likely to be the most cost effective.

Most polymer of acrylamide are soluble in water under virtually all conditions & tolerate, moderate amounts of salts or other additives. Hydrophilic, but insoluble gels can be prepared.

Polymers can be tailored for specific use by introduction of the ionic groups and by adjustment of molecular weight.

Polymer molecules bond to many solid surfaces and dissolved species.

## Experiment No.1

### Object

To prepare a 10% solution of Polyacrylamide by solution polymerization technique.

### Recipe

	<b>Materials</b>	<b>Quantities (gm.)</b>
1.	DM Water	875.00
2.	Acrylamide	99.00
3.	Potassium per sulphate	0.645
4.	DM water	10.000
5.	AIBN	0.180
6.	DM Water	15.175
		<hr/>
		<b>1000.000</b>
		<hr/>

### Procedure

1. Take DM water into reaction kettle and start agitation
2. Heating start slowly and maintain the temperature at 74°C.
3. Add acrylamide and continue stir till the complete dissolution.
4. Further maintain the temperature 72-74°C.
5. Prepare the PPS solution (3+4) and add into the reaction kettle.
6. Reaction will take place. Temperature will increase nearly Upto 80-82°C.
7. After reaching maximum temperature, hold the batch for 150 minutes at 80-82°C.

8. After completion of the holding, add AIBN solution, 5+6, and further hold for 1 hour.
9. Stop heating. Cool down to below 40°C.

### **Observation**

#### **Solid Content, %**

1. Wt. Of foil	2.6752 gm.
2. Wt. Of sample	3.5020 gm.
3. Wt. OF dry sample+ foil	3.0555 gm.
4. Wt. Of dry sample	0.3803 gm.

**% age solid content = 11.190 %**

**pH value = 7.54**

**Brookfield Viscosity = 56 poise**

### **Result**

We got a clear viscous solution of Polyacrylamide, whose solid contents is 11.190%, pH value 7.54 & viscosity is 56 poise.

## Experiment No.2

### Object

To prepare a PVOH assisted Polyacrylamide solution-by-solution polymerization technique.

### Recipe

	<b>Materials</b>	<b>Quantities (gm.)</b>
1.	DM Water	300.00
2.	GH-17, PVOH	30.00
3.	Acrylamide	70.000
4.	DM water	600.00
5.	PPS	1.000
6.	DM Water	30.00
		<hr/>
		<b>1031.000</b>
		<hr/>

### Procedure

1. Take DM water into reaction kettle and start agitation
2. Add GH-17 into reaction kettle.
3. Heating start slowly and maintain the temperature at 88-90°C.
4. Hold the batch for 1 hour.
5. Prepare a solution of acrylamide & DM water in a separate beaker.

6. At 80-82°C, add PPS solution into the kettle, and start the feeding of the acrylamide solution.
7. Total feeding time would be 1-1 ½ hour.
8. Reaction temperature would be 82-84°C.
9. After feeding hold for 1 hour at same temperature.
10. After completion of the holding, cool it to 40°C.

## **Observation**

### **Solid Content, %**

1. Wt. Of foil	1.3961 gm.
2. Wt. Of sample + foil	3.1480 gm.
3. Wt. OF dry sample+ foil	1.5704 gm.

**% age solid content = 9.949 %**

**pH value = 7.23**

**Brookfield Viscosity = 22 poise**

## **Result**

We get a clear viscous solution of PVOH assisted Polyacrylamide, whose solid contents are 9.949 %, pH value 7.23 & viscosity is 22 poise.

## Experiment No.3

### Object

To prepare a N-Methylol Acrylamide (NMA) solution. (ICR-274)

### Recipe

	<b>Materials</b>	<b>Quantities (gm.)</b>
1.	DM Water	12.535
2.	Acrylamide	16.900
3.	Formaline	10.010
4.	10% NaOH solution	0.060
5.	10% H <sub>2</sub> SO <sub>4</sub> solution	0.060
		<hr/>
		<b>39.565</b>
		<hr/>

### Procedure

1. Take DM water into a beaker.
2. Heating start slowly and maintain the temperature at 40-60°C.
3. Add acrylamide into DM water, while continuous stirring.
4. After complete dissolution, add Formaline into beaker
5. Prepare the PPS solution (3+4) and add into the reaction kettle.
6. Maintain temperature 20-22°C.
7. Add 10% solution of NaOH. Temperature will increase. (pH 10.5-11.000)
8. Maintain temperature at 20-22°C.
9. Stir for 45 minutes.

10. Adjust pH by 10% H<sub>2</sub>SO<sub>4</sub> solution.

### **Observation**

#### **Solid Content, %**

1. Wt. Of foil	2.6752 gm.
2. Wt. Of sample	3.5020 gm.
3. Wt. OF dry sample+ foil	3.0555 gm.
4. Wt. Of dry sample	0.3803 gm.

**% age solid content = 11.190 %**

**pH value = 7.54**

**Brookfield Viscosity = 56 poise**

### **Result**

We got a clear viscous solution of Polyacrylamide, whose solid contents is 11.190%, pH value 7.54 & viscosity is 56 poise.



## Experiment No.4

### Object

To prepare a (80+ 20) solution co-polymer of Acrylamide & N-Methylol Acrylamide (NMA) by solution polymerization technique.

### Recipe

	<b>Materials</b>	<b>Quantities (gm.)</b>
1.	DM Water	854.00
2.	Acrylamide	80.00
3.	NMA	40.00
4.	PPS	0.645
5.	DMW	10.000
6.	AIBN	0.180
7.	DMW	15.175
		<hr/>
		<b>1000.000</b>
		<hr/>

### Procedure

1. Take DM water into reaction kettle and start agitation.
2. Heating start slowly and maintain the temperature at 74°C.
3. Add acrylamide and NMA continue stir till the complete dissolution.
4. Further maintain the temperature 72-74°C.
5. Prepare the solution of PPS and DMW and add into the reaction kettle at 72-74°C

6. Reaction will take place and temperature will increase till 80°C
7. Hold the batch for 2 ½ hour.
8. Add AIBN & DMW into reaction kettle.
9. Further hold for 1 hour.
10. Stop heating. Cool down to below 40°C.

## **Observation**

### **Solid Content, %**

1. Wt. Of foil	1.4103 gm.
2. Wt. Of sample	2.4634 gm.
3. Wt. OF dry sample+ foil	1.6784 gm.

**% age solid content = 10.88 %**

**pH value = 4.54**

**Brookfield Viscosity = 152 poise**

## **Result**

We get a clear viscous solution of Polyacrylamide+ NMA, whose solid contents is 10.88 %, pH value 4.54 & viscosity is 152 poise.

## Experiment No.5

### Object

Reactive Dyeing of cotton fabric with the help of polymeric auxiliaries by pad dry cure method

### Material required

	Materials	Quantities (gm.)
1.	PAM 10% sol	50.00
2.	PVOH assisted PAM	50.00
3.	PAM+NMA	2×50.00
4.	DMDHEU	5.00
5.	Procion Red M5B	5×0.1
6.	Cotton	5×5
7.	DMW	500

### Procedure

#### Pretreatment of Cotton samples

1. Ist prepares 5 piece of cotton, 5 gm each.
2. Now take 5 beakers.

Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 5
50 gm PAM	50 gm PVOH assisted PAM	50 gm PAM+NMA	50 gm PAM+NMA + 5 gm of 50% sol. DMDHEU	Water

**Table: ingredients used in pretreat the cotton samples**

3. Dip the cotton pieces into respective beakers.
3. Hold for 15 minutes.
4. Now pad the pretreated cotton pieces on padding machine at 40-rpm/20 psi pressure.
5. Then dry the samples at 150°C for 7 minutes in oven.
6. Pretreated samples are ready for dyeing.

### **Pad dry cure Dyeing**

1. Take 500 gm of DM water into a beaker.
2. Add .5 gram of Red M5B into that beaker, stir properly.
3. Now distribute the dyebath in to 5 beakers, 100 gm each.
4. Dip the respective cotton samples in respective beakers.
5. Hold the samples for 15 minutes.
6. Now pad it by two-dip two-nip technique on padding machine at 40rpm/ 20psi.
7. First dry at ambient temperature, and then cure at 150°C for 7 minutes in oven.
8. Now first give the cold-water wash to the samples.
9. Then hot water wash & finally surf wash.
10. Cure at 150°C for 7 minutes in oven.

## Experiment No.6

### Object

Reactive Dyeing of cotton fabric with the help of polymeric auxiliaries by exhaust dyeing method.

### Material required

	Materials	Quantities (gm.)
1.	PAM 10% sol	50.00
2.	PVOH assisted PAM	50.00
3.	PAM+NMA	2×50.00
4.	50% sol. of DMDHEU	5.00
5.	Procion Red M5B	5×0.1
6.	Cotton	5×5
7.	DMW	500

M: L Ratio = 1:20

### Pretreatment of Cotton samples

Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 5
50 gm PAM	50 gm PVOH assisted PAM	50 gm PAM+NMA	50 gm PAM+NMA + 5 gm DMDHEU	Water

**Table: ingredients used in pretreat the cotton samples**

## Procedure

1. Ist prepares 5 piece of cotton, 5 gm each.
2. Now take 5 beakers.
3. Dip the cotton pieces into respective beakers.
4. Hold for 15 minutes.
5. Now pad the pretreated cotton pieces on padding machine at 40-rpm/20 psi pressure.
6. Then dry the samples at 150°C for 7 minutes in oven.
7. Pretreated samples are ready for dyeing.

## Exhaust Dyeing

1. Take 500 gm of DM water into a beaker.
2. Add 0.5 gram of Red M5B into that beaker, stir properly.
3. Now distribute the dyebath in to 5 beakers, 100 gm each.
4. Dip the respective cotton samples in respective beakers.

Time	Material
Starting time	Dip the pretreated cotton samples in beakers
0-210 minutes	Continuous stirring of dyebath

5. Total dyeing time was 210 minutes.
6. Now first give the cold-water wash to the samples.
7. Then hot water wash & finally surf wash. & Cure at 150°C for 7 minutes in oven.

## Experiment No.7

### Object

Pretreatment of cotton for making it cationized & then reactive dyeing by exhaustion method.

### Material required

#### For Pretreatment of Cotton

Sample 1	Sample 2	Sample 3
1. Choline Chloride: 5 gm 2. 50% sol. of DMDHEU: 5gm 3. DM Water: 90 gm	1. Pidicron (Cationic Agent): 2.5 wt.% of the cotton	Untreated

#### For Dyeing of Pretreated Cotton samples by exhaustion method

Sample 1	Sample 2	Sample 3 (Std.)
Red M5B: 0.1 gm	Red M5B: 0.1 gm	Red M5B: 0.1 gm
NaCl: -----	NaCl: -----	NaCl: 5 gm.
NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm	NaHCO <sub>3</sub> : 0.5 gm
Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.
DM Water: 100 gm	DM Water: 100 gm	DM Water: 100 gm

**Table: Ingredients used in Pretreated the Cotton samples**

Cotton samples: 3 (5 gm each)

M: L Ratio of Dye bath = 1:20

Dyeing temperature: 60°C throughout the dyeing

## **Procedure**

### **Pretreatment of Cotton samples**

1. Take 3 beakers & make the solutions for pretreatment.
2. Dip the cotton pieces into respective beakers.
3. Hold for 15 minutes.
4. Now pad the pretreated cotton pieces on padding machine at 40-rpm/20 psi pressure.
5. Then dry the samples at 150°C for 7 minutes in oven.
6. Pretreated samples are ready for dyeing.

### **Exhaust Dyeing**

1. Take 300 gm of DM water into a beaker.
2. Add 0.3 gram of Red M5B into that beaker & stir it properly.
3. Now distribute the dyebath in to 3 beakers, 100 gm each.
4. Increase the temperature to 60°C. Maintain the same temperature throughout the dyeing period.
5. Dip the respective cotton samples in respective beakers.



S.No.	Time(min)	Sample 1	Sample 2	Sample 2
1.	Starting	Dip the samples.	Dip the samples	Dip the samples
2.	10	-----	-----	NaCl: 2.5 gm
3.	10	-----	-----	NaCl: 2.5 gm
4.	20	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.
5.	130	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.
6.	30	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C
7.	-----	Wash & rinse in cold water	Wash & rinse in cold water	Wash & rinse in cold water
8.	-----	Wash & rinse in HOT water	Wash & rinse in HOT water	Wash & rinse in HOT water
9.	-----	Surf washing	Surf washing	Surf washing

**Table: Dyeing Cycle**

Total dyeing time was 200 minutes.

## Experiment No.8

### Object

Cationization of cotton (NaOH pretreated) & then reactive dyeing by exhaustion method.

### Material required

#### For Pretreatment of Cotton

#### 10% Solution: NaOH

Sample 1	Sample 2	Sample 3	Sample 4
1. Choline Chloride: 10 gm 2. DM Water: 40 gm	1. Choline Chloride: 10 gm 2. NaCl: 15gm 3. DMW: 25 gm.	1. Choline Chloride: 10 gm. 2. DMDHEU: 5 gm 3. DMW: 35gm.	1. Choline Chloride: 10 gm. 2. DMDHEU: 10 gm 3. DMW: 30gm.

#### For Dyeing of Pretreated Cotton samples by exhaustion method

Sample 1	Sample 2	Sample 3	Sample 3
Red M5B: 0.1 gm	Red M5B: 0.1 gm	Red M5B: 0.1 gm	Red M5B: 0.1 gm
NaCl: -----	NaCl: -----	NaCl: -----	NaCl: -----
NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm	NaHCO <sub>3</sub> : 0.5 gm	NaHCO <sub>3</sub> : 0.5 gm
Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.
DM Water: 100 gm	DM Water: 100 gm	DM Water: 100 gm	DM Water: 100 gm

Cotton samples: 4 (5 gm each)

M: L Ratio of Dyebath = 1:20

Dyeing temperature: 60°C throughout the dyeing

## **Procedure**

### **Pretreatment of Cotton samples**

1. Make a 10% NaOH solution & dip the cotton samples into for 2 hours.
2. Now pad the cotton pieces on padding machine at 40-rpm/20 psi pressure & dry it at ambient temperature.
3. Now make the solution for pretreatment.
4. Dip the cotton pieces into respective beakers.
5. Hold for 15 minutes.
6. Now pad the pretreated cotton pieces on padding machine at 40-rpm/20 psi pressure.
7. Then dry the samples at 150°C for 7 minutes in oven.
8. Pretreated samples are ready for dyeing.

### **Exhaust Dyeing**

1. Take 400 gm of DM water into a beaker.
2. Add 0.4 gram of Red M5B into that beaker & stir it properly.
3. Now distribute the dyebath in to 4 beakers, 100 gm each.

4. Increase the temperature to 60°C. Maintain the same temperature throughout the dyeing period.
5. Dip the respective cotton samples in respective beakers.

<b>Time (min)</b>	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>	<b>Sample 4</b>
Starting	Dip the samples.	Dip the samples	Dip the samples	Dip the samples.
10	NaCl -----	NaCl -----	NaCl: -----	NaCl -----
10	NaCl-----	NaCl -----	NaCl: -----	NaCl -----
20	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.
130	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.
30	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C
-----	Wash & rinse in cold water	Wash & rinse in cold water	Wash & rinse in cold water	Wash & rinse in cold water
-----	Wash & rinse in HOT water	Wash & rinse in HOT water	Wash & rinse in HOT water	Wash & rinse in HOT water
-----	Surf washing	Surf washing	Surf washing	Surf washing

**Table: Dyeing Cycle**

Total dyeing time was 200 minutes.

## Experiment No.9

### Object

Cationization of cotton & then reactive dyeing by exhaustion method.

### Material required

#### For Pretreatment of Cotton

Sample 1	Sample 2	Sample 3	Sample 4
1. Choline Chloride: 10 gm 2. DM Water: 40 gm	1. Choline Chloride: 10 gm 2. Na <sub>2</sub> SO <sub>4</sub> : 15gm 3. DMW: 25 gm.	1. Choline Chloride: 10 gm. 2. 50% solution DMDHEU: 5 gm 3. DMW: 35gm.	1. Choline Chloride: 10 gm. 4. 50% solution DMDHEU: 10 gm 2. DMW: 30gm.

#### For Dyeing of Pretreated Cotton samples by exhaustion method

Sample 1	Sample 2	Sample 3	Sample 3
Red M5B: 0.1 gm	Red M5B: 0.1 gm	Red M5B: 0.1 gm	Red M5B: 0.1 gm
NaCl: -----	NaCl: -----	NaCl: -----	NaCl: -----
NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm	NaHCO <sub>3</sub> : 0.5 gm	NaHCO <sub>3</sub> : 0.5 gm
Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.
DM Water: 100 gm	DM Water: 100 gm	DM Water: 100 gm	DM Water: 100 gm

Cotton samples: 4 (5 gm each)

M: L Ratio of Dyebath = 1:20

Dyeing temperature: 60°C throughout the dyeing

## **Procedure**

### **Pretreatment of Cotton samples**

1. Ist make the 4 solutions in 4 separate beakers for pretreatment.
2. Dip the cotton pieces into respective beakers.
3. Hold for 15 minutes.
4. Now pad the pretreated cotton pieces on padding machine at 40-rpm/20 psi pressure.
5. Then dry the samples at 150°C for 7 minutes in oven.
6. Pretreated samples are ready for dyeing.

### **Exhaust Dyeing**

1. Take 400 gm of DM water into a beaker.
2. Add 0.4 gram of Red M5B into that beaker & stir it properly.
3. Now distribute the dyebath in to 4 beakers, 100 gm each.
4. Increase the temperature to 60°C. Maintain the same temperature throughout the dyeing period.
5. Dip the respective cotton samples in respective beakers.

<b>Time (min)</b>	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>	<b>Sample 4</b>
Starting	Dip the samples.	Dip the samples	Dip the samples	Dip the samples.
10	NaCl -----	NaCl -----	NaCl: -----	NaCl -----
10	NaCl-----	NaCl -----	NaCl: -----	NaCl -----
20	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.	NaHCO <sub>3</sub> : 0.5 gm.
130	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.	Na <sub>2</sub> CO <sub>3</sub> : 0.07 gm.	Na <sub>2</sub> CO <sub>3</sub> :0.07gm.
30	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C	Pad & cure in oven at 150°C
-----	Wash & rinse in cold water	Wash & rinse in cold water	Wash & rinse in cold water	Wash & rinse in cold water
-----	Wash & rinse in HOT water	Wash & rinse in HOT water	Wash & rinse in HOT water	Wash & rinse in HOT water
-----	Surf washing	Surf washing	Surf washing	Surf washing

**Table: Dyeing Cycle**

Total dyeing time was 200 minutes.

## Results & Discussions

We prepare three types of Polyacrylamide solutions, namely:

1. 10% Solution of Polyacrylamide
2. 10% solution of Polyvinyl alcohol assisted Polyacrylamide
3. 10% solution of the Co-Polymer of Acrylamide & NMA.

The mechanism of fixation of reactive dyes on Polyacrylamide treated and partially cross-linked cotton fabric is as follows:

Cotton fabric treated with Polyacrylamide & cross-linking agents demonstrate the introduction of a highly nucleophilic amino group. (-NH<sub>2</sub>) in the cellulosic chain. The cationic charged amino groups may be involved in the adsorption of the anionic chromophore of reactive dyes. The higher dye uptake may be postulated to be due to the presence of the (-CONH<sub>2</sub>) groups available from polyacrylamide, which also improves the reactivity of the cellulosic substrate. The attachment of the dye molecule on the partially modified cellulose substrate is found to be tough covalent bonding as no dye stripes out from dyed sample in pyridine (100%) as well as in its mixture with water (50:50).

An attempt has been made in the present investigation to commercialize this neutral dyeing of reactive dyes on cotton. For this purpose we had take Red M5B, Procion Cold Brand Reactive dye for salt

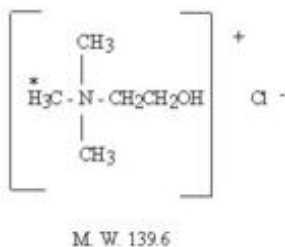


free neutral reactive dyeing purpose. Then we compare the results of dyeing samples, with the conventional process.

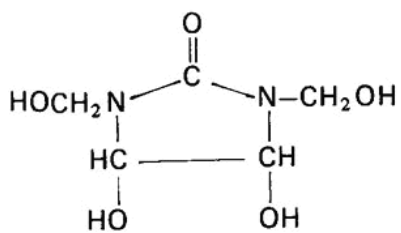
Cellulose cross-linking is a very important textile chemical process, and is the basis for a vast array of durable press- and crease resistance finished textile products. N Methylol cross linkers containing formaldehyde give fabrics describable properties of better reactivity of cotton with reactive dyes.

But unfortunately we didn't get very impressive results with Polyacrylamide, PVOH assisted Polyacrylamide & Co polymer of NMA & Acrylamide along with the cross linkers.

Then we change our approach & work to improve the affinity of anionic dyes for cotton is to add cationic dye sites to the fiber. We knew that **Cotton & Dye both are anionic in nature.** That's why we use salt to make it easier for dye to make a reactive bond with the cotton. So we think that if we could make cotton cationized by pretreated it, then we can easily make the reactive bond between dye & cotton. Then we use the quaternary cationic compound Choline Chloride along with a cross linker DMDHEU.



### Choline Chloride



DMDHEU

### **Di-methylol dihydroxy ethylene urea (DMDHEU)**

Here I am very glad to announce that the results comes by using **Choline Chloride** along with **Di-methylol dihydroxy ethylene urea (DMDHEU)** was very very impressive. Or in other words, we achieve the target of salt free reactive dyeing of Cotton textiles.

## **Result of Experiment No 5**

In this practical we use all three types of PAM, which we make in batch reactor for our salt free dyeing purpose, and then dyed the pretreated cotton samples with pad dry cure method. But unfortunately we didn't get good results.

1. 50 gm PAM
2. 50 gm PVOH assisted PAM
3. 50 gm Copolymer of PAM + NMA
4. 50 gm Copolymer of PAM+NMA, + 5 gm DMDHEU
5. Untreated

## **Results of Experiment No. 6**

In this experiment we take the same concentrations of dye, PAM & cross linker as we take in the experiment No. 5, but this time we adopt the exhaustion technique of dyeing. As results once again was not so much good.

1. 50 gm PAM
2. 50 gm PVOH assisted PAM
3. 50 gm Copolymer of PAM + NMA
4. 50 gm Copolymer of PAM+NMA, + 5 gm DMDHEU
5. Untreated

## **Result of Experiment No. 7**

In this practical first time we approach the Cationization of cotton concept. For this purpose we use the low molecular weight quaternary compound Choline Chloride along with DMDHEU. Then dyed the pretreated cotton by exhaustion technique. This method is totally salt free. Fortunately this time we get very impressive results.

1. Pretreated with Choline Chloride & DMDHEU
2. Pretreated with Cationic agent PIDICRON (Reported by Professor Chavan, IIT Delhi) in Proceeding of International conference on emerging trends in polymers & textiles, January'2005.
3. Untreated

## **Results of Experiment No 8.**

In last experiment, as I report earlier that the best results came in CC/DMDHEU sample, so this time we try to mercerized the cotton before pretreatment, & than repeat the Experiment No. 7 again.

Mercerization, with NaOH is a reported method for better dye uptake from the dyebath. Unfortunately this time we didn't get so much impressive results as we get in unmercerized cotton samples.

1. Mercerized with NaOH & Pretreated with Choline Chloride & DMDHEU
2. Mercerized with NaOH & than Pretreated with Cationic agent PIDICRON (Reported by Professor Chavan, IIT Delhi) in Proceeding of International conference on emerging trends in polymers & textiles, January'2005.
3. Untreated

## **Results of Experiment No 9**

This time again we use CC/DMDHEU, & take the different quantities of CC/DMDHEU. We take 4 samples of cotton, & pretreated it with CC/DMDHEU. The results of these experiments are given below: -

1. CC 10 gm & DMW 40 gm
2. CC 10 gm & Na<sub>2</sub>SO<sub>4</sub> 15 gm, DMW 25 gm
3. CC 10 gm, DMDHEU 5 gm, DMW 35 gm.
4. CC 10 gm, DMDHEU 10 gm, DMW 30 gm

## **Conclusion**

Cotton treated with a reactant (Choline Chloride) that provides cationic dye sites to cotton without electrolytes & cross linker DMDHEU, which plays a very positive role in making cellulose-dye reactive bond, give excellent colour yields with Procion Red M5B reactive dye. The dyeing procedure, which we adopt for dyeing, was exhaust-dyeing method.

By using proposed procedure of salt free & slightly basic reactive dyeing, we can decrease the percentage of the hazardous metal ions from the effluent, which is very harmful to the fertility of the soil as well as very harmful to the ground water too.



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